A Study of Translational Diffusion Constants of Paramagnetic Species In Solution

by

Hasan Bakor Abdullah Balkhoyor

A Thesis Presented to the

FACULTY OF THE COLLEGE OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

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This thesis, written by **HASAN BAKOR BALKHOYOR** under the direction of his Thesis Advisor and approved by his Thesis Committee, has been presented to and accepted by the Dean of the College of Graduate Studies, in partial fulfillment of the requirements for the degree of ***MASTER OF SCIENCE in Chemistry.***

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THIS THESIS IS DEDICATED TO MY

PARENTS,

WIFE,

and

CHILDREN.

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TABLE OF CONTENTS

CHAPTER 2. APPARATUS

CHAPTER 3. PROCEDURE

LIST OF TABLES

LIST OF FIGURES

خلاصة الرسالة

اسم مقدم الرسالة : حسن بكر عبدالله بالخير

عنوان الرسالة : دراسة معامل الانتشار الانتقالي للمركبات ذات الخواص المغناطيسية في المحاليل

التخصص : الكيمياء الفيزيائية

تاريخ التقديم : يوم الثلاثاء ٢ محرم ١٤١٤ هجرية

في هذا البحث تمت دراسة معامل الانتشار الانتقالي لمركبين لهما خواص مغناطيسية ، الاول : ثنائي كلورو - اثنين(η- بنتاداينيل حلقي) فاناديوم ، ويختصر (Cp_2VCl_2) في الكلوروفورم كمذيب، والثاني : S - ميثيل - N - ٥ - مثوكسي - ساليسيليدين - هايدرازين - كاربودايثيوتو - فنانثرولين - اكسي الفاناديوم ، ويختصر VO[5-MeO Sal SB] (Phen)، في ثنائي كلورو ميثان كمذيب. وذلك عند درجة حرارة الغرفة. وقد استخدمت طريقة الانتشار خلال الانبوب الشعرية لأيجاد هذه المعاملات عن طريق تتبع شدة الطيف المغناطيسي مع مرور الزمن بواسطة جهاز طيف الطنين المغناطيسي الأكتروني . وبرسم علاقة التغير بين الزمن وشدة الطيف ثم ايجاد افضل منحنى نظري يحاكي المنحنى التجريبي من خلال حل القانون الأنتشار الثاني ل- Fick'S والتعويض في هذا القانون لأيجاد المعاملات بواسطة برنامج كمبيوتر كتب لهذا الغرض. وبأستخدام علاقة Stokes - Einstein التي تربط بين معامل الأنتشار الأنتقالي و اللزوجة وجد نصف القطر الحركي للجزيئات ومنه حسبت حجوم هذه الجزيئات. فكان معامل الأنتشار الأنتقالي للمركب الأول $0.520x10^{-5}$ سم^2/ث ، وحجمه $250x10^{-8}$ سم^3 .ومعامل الأنتشار للمركب الثاني $655x10^{-5}$ سم^2/ث وحجمه $275x10^{-8}$ سم^3 .

في الجزء الثاني من الرسالة استخدمت اربع مجموعات مختلفة لمعاملات مغناطيسية للمركب الأول ذكرت في الدوريات العالمية لتحقيقها على قيم عرض الخطوط للطيف المغناطيسي عند درجات حرارة مختلفة في مادة التولوين ، لأيجاد معامل التباين الدوراني (N) وكذلك محور الدوران لهذا المركب. وقد وجد ان مجموعة واحدة من المعاملات المغناطيسية حققت قيم عرض خطوط الطيف المغناطيسي بمعامل تباين دوراني (N) = 2.7 ± 0.5 وذلك على المحور Z' = Y ، و تطابقت هذه القيمة مع نموذج Stokes-Einstein و معادلة القيمة المأنونة (Allowed - Values Equation). و من معامل التباين الدوراني حسب زمن الدوران الذي يرتبط بعلاقة رياضية مع اللزوجة والحرارة و الحجم الجزيئي ومعامل التجاذب بين جزيئات المذاب و المذيب (k) ، الذي حسبت قيمته 0.15 . وهذه القيمة تدل على ان المركب اكثر انزلاق من المركب النموذجي فنادايل اسيتونات VOAA (والذي يبلغ مقدار التجاذب له في التولوين 0.53 ، ويؤيد ذلك معامل الألتصاق (S) الذي يأخذ القيم ($0 < S < 1$) فعندما يكون S يساوي صفر فذلك يدل على الأنزلاق الكامل ، والواحد الألتصاق الكامل ، وبحساب معامل الألتصاق للمركب الأول وجد ان قيمته 0.0875 . وبمراجعة اشكال هذه الجزيئات يمكن تقدير ذلك فكلما كان الجزيئ منتظما قل معامل التجاذب بين جزيئات المذيب والمذاب وكذلك قل معامل الألتصاق ، والعكس كلما كان الشكل الجزيئ غير منتظم ازداد معامل التجاذب و كذلك معامل الألتصاق .

ABSTRACT

The translational diffusion constants of two paramagnetic species, dichlorobis(η-cyclopentadienyl)vanadium, abbrevuated as (Cp_2VCl_2) in chloroform, and S-methyl-N-5-methoxy-salicylidenehydrazine-carbodithioatophenanthroline-oxovnadium(IV), abbreviated as VO[5-MeO-Sal SB](Phen) in methylene chloride were measured at room temperature (25±1 ^{0}C) by a capillary diffusion method. The translational diffusion processes were monitored by electron spin resonance spectral intensities as a function of time. The total spectral intensities were plotted as a function of time and from the best least squares fit a single value of the translational diffusion coefficient was obtained. A computer program based on Fick's second law of diffusion for the capillary diffusion cell has been written to get a single value of the diffusion constant. Using Stokes-Einstein for translational diffusion, the hydrodynamic radii and the molecular hydrodynamic volumes of the two paramagnetic species in solution were found to be 0.520×10^{-5} and 0.655×10^{-5} cm^2/s, and 250 and 275 Å^3, respectively.

From an analysis of the temperature dependent ESR line widths of Cp_2VCl_2 in toluene in the motional narrowing region by using four sets of the magnetic parameters available in the literature, only the set by Peterson and Dahl could explain the line width data. It was found that Cp_2VCl_2 was undergoing anisotropic reorientation with $N = 2.7 \pm 0.5$ at an axis z' = Y, where N is the ratio of $R_\parallel/R_\perp$ and $R_\parallel$ is the rotational diffusion constant along the molecular Z axis and $R_\perp$ is the rotational diffusion constant perpendicular to the molecular Z axis. This value is supported by the Stokes-Einstein model and the allowed-values equation.

In addition, the rotational correlation times as a function of temperature were determined from the line width data. The anisotropic interaction parameter κ, determined from the plot of τ_1 vs η/T was found to be 0.150 . The anisotropic interaction parameter is a measure of the anisotropy of intermolecular interactions. The values show that Cp_2VCl_2 in toluene is more slip than VOAA in toluene which is more stick and its κ is 0.53 . The Stickiness factor (S) is calculated to be 0.0875 for Cp_2VCl_2 which is close to the slip limit (S=0). Therefore, it seems that κ value decreases with decreasing solute corrugation.

CHAPTER ONE

INTRODUCTION

CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

The purpose of this research is to study the translational motion of two paramagnetic species in solution by the capillary diffusion method. The first complex is **S-methyl-N-5-methoxy salicylidene hydrazine carbodithioatophenathroline oxovanadium(IV)**, in methylene chloride, written simply as, **VO[5-MeO-Sal SB](Phen)**, which has a monomeric octahedral structure as shown in Fig.(1.1) [1]. The second complex is **dichlorobis(η-cyclopentadienyl)vanadium** in chloroform, written as $Cp_2^1VCl_2^1$, its structure shown in Fig.(1.2). The translational motion will be measured at room temperature by a capillary diffusion method [2,3,4,5]. It has been previously shown that the translational diffusion processes can be monitored by electron spin resonance spectral intensities as a function of time [6]. The total spectral intensities are plotted as a function of time and from the best least-squares fit a single value of translational diffusion coefficient can be obtained [3]. Using the Stokes-Einstein equation the hydrodynamic radii of the two paramagnetic species in solution can be calculated.

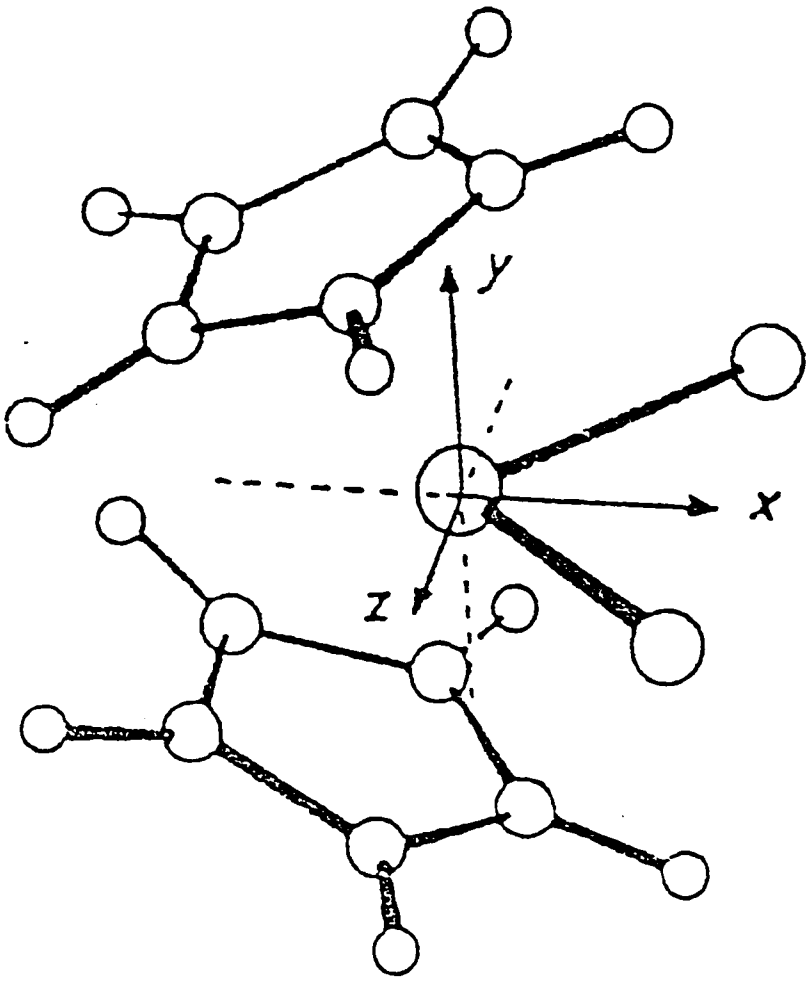

Fig. 1.1: Cp_2VCl_2

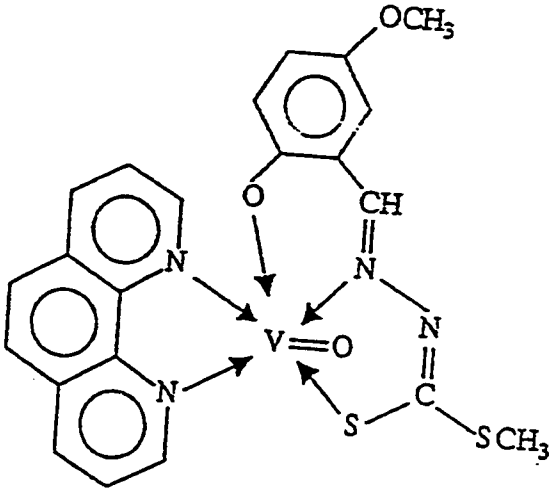

Fig. 1.2: VO[5-MeO-Sal SB](Phen)

The translational diffusion coefficient D is related to the viscosity by the Stokes-Einstein equation

$$D = \frac{kT}{6\pi\eta r_o} \qquad (1.1)$$

where k is the Boltzmann constant, T is the absolute temperature, η is the shear viscosity, and r_0 is the hydrodynamic radius of an equivalent spherical volume [7], from which the molecular volume of the paramagnetic species can be determined. In the past the molecular volume has been determined using the Dreiding model [8], a computer program (Desktop Molecular Modeller) [1], and experimentally using such techniques as the porous disk method [9], and the electron spin resonance/spin exchange method [10].

The value of r_0 which determined experimentally by the capillary diffusion method will be used in recalculating the κ value from the correlation time, τ_R, which is analyzed from molecular reorientation of paramagnetic species in solution as a function of temperature [1]. For spherical top or linear molecule this correlation time can be expressed as [11],

$$\tau_R = \left(\frac{4\pi r_o^3}{3}\right)\left(\frac{\kappa}{k_B}\right)\left(\frac{\eta}{T}\right) \qquad (1.2)$$

Where η is the coefficient of shear viscosity of the solvent [12], and κ is an experimentally determined dimensionless coupling parameter called the anisotropic interaction parameter which measures the coupling of rotational motions of the probe to the translation modes of the fluid [11].

From the electron spin resonance relaxation studies [13], which have been analyzed in terms of the hydrodynamic free space model for molecular relaxation in liquids at various microwave frequencies [8,13,14], the analysis of the temperature dependent ESR line shapes in the motional narrowing and slow tumbling regions, the stickiness factors S were measured [15].

The stickiness factor is independent of molecular geometry and is zero in the slip and one in the stick limit, $0 < S < 1$. The stickiness factor can be calculated from the relationship

$$S = \frac{\kappa - C_{slip}^{hyd}}{1 - C_{slip}^{hyd}} \qquad (1.3)$$

where C_{slip}^{hyd} is the empirical factor which depends on the non-hydrodynamic character of the friction and on the shape of the probe molecules [11], then from the recalculated value of κ we can obtain a more accurate value of S.

In the remainder of this chapter we give an overview of the transport process. The state of a system under diffusion is defined, then Fick's law of diffusion is set up mathematically and a solution of this law is derived. In Chapter II the apparatus used and its function in the experiment are described. In Chapter III we describe the experimental procedure used to set up the capillary diffusion cell using the ESR technique. In Chapter IV the analysis of the paramagnetic parameters are given . In Chapter V the conclusions of the experimental results and discussion are given.

1.2 TRANSPORT PHENOMENA

Transport phenomenon arises because any system in nonequilibrium will always try to approach equilibrium.
A system is in equilibrium if the intensive state variables or parameters (temperature and density, for example) are constant at all times and have the same magnitude at all positions in the system.

From this definition follow other familiar properties of equilibrium state: at equilibrium, *gradients* of the parameters are absent, spontaneous processes do not occur, and there is no net exchange of matter or energy between the system and the surroundings, or between one part of the system and another.

If a system is in a state in which these conditions are not satisfied, the system is in nonequilibrium state. Suppose an equilibrium system is perturbed to a nonequilibrium state by some external or internal disturbance. At least one of the system parameters becomes a function of position. When the disturbance is removed, an irreversible decay process occurs spontaneously, and the system advances through a series of nonequilibrium state until equilibrium is reached.

The decay process is a transport process, the name arising because some quantity is transferred throughout the system as the system attempts to make all parameters independent of position.

A spatial dependence of the parameters is thus associated with a *flux* of some kind. It is logically assumed that the relation between a gradient X and its conjugate flux J is linear thus,

$$J = L X \tag{1.4}$$

If Eq. (1.4) is valid at all times, the system is said to be "close to equilibrium" at all times.

The rate at which the system approaches equilibrium is determined by the proportionality constant of Eq.(1.4) that is by the *transport coefficient* L.

It is a matter of experience that transport processes taking place in a system with n independent gradients can be represented by the relation,

$$J = \sum_{k=1}^{n} L_{ik} X_k \qquad (i=1,2,3,\ldots,n) \qquad (1.5)$$

In the nomenclature of nonequilibrium thermodynamics, X is called a thermodynamic driving force, and L a phenomenological coefficient.

Equation (1.5) can be written in matrix notation,

$$\begin{bmatrix} J_1 \\ J_2 \\ \cdot \\ \cdot \\ \cdot \\ J_n \end{bmatrix} = \begin{bmatrix} L_{11} & L_{12} & \cdot & \cdot & \cdot & L_{1n} \\ L_{21} & L_{22} & \cdot & \cdot & \cdot & L_{2n} \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ L_{n1} & L_{n2} & \cdot & \cdot & \cdot & L_{nn} \end{bmatrix} \begin{bmatrix} X_1 \\ X_2 \\ \cdot \\ \cdot \\ \cdot \\ X_n \end{bmatrix}$$

which expresses the fact that if the off-diagonal elements of L exist, then the ith flux depends in a linear manner on the kth force as well as on its conjugate X_i. The relation between J_i and X_k is called thermodynamic coupling.

1.2.1 Uncoupled Transport Processes

When $L_{ik} = 0$ $(i \neq k)$, Eq.(1.5) becomes $J_i = L_{ii}X_i$, a phenomenological representation of familiar empirical laws,

(1) Fourier's law of heat conduction,

$$q = -\lambda \nabla T \tag{1.6}$$

The vector q is the heat flux, the coefficient λ is the coefficient of thermal conductivity, and grad T is the gradient of temperature.

(2) Fick's law of diffusion,

$$J_i = - D \nabla C_i \tag{1.7}$$

where J_i is the flux of chemical species i , C_i is the concentration of i, and D is the diffusion coefficient.

(3) Newton's law of viscosity,

$$\Pi_{yx} = -\eta \frac{\partial U_x}{\partial y} \qquad (1.8)$$

Here Π_{yx} represents a momentum flux in the y direction caused by a fluid flow in the x direction with velocity component U_x , η is the coefficient of shear viscosity [16].

1.2.2 Coupled Transport Processes

The coupled phenomena arising if $L_{ik} \neq 0$, *thermal diffusion* of gases is an example of this processes in which the diffusion of gases depends not only on the concentration difference but also on the temperature difference. Also the *thermoelectricity* with coupling between flows of heat and of electrical current is another example [16].

1.2.3 Continuous and Discontinuous System

The fluid can be regarded as a continuum and the intensive state variables as continuous function of space and time. Such a system is called continuous. Also the phenomenological or transport coefficients, for both coupled and single processes, appertain to the fluid itself. At a microscopic level they could be described by the temperature

and pressure of the system, together with the microscopic properties of the components of the fluid, for example by the molecular dimensions and the intermolecular potential function, *thermal diffusion* is an example here for continuous system in which the vessel plays no part in the effect apart from containing the fluid. In a discontinuous system, the vessel plays an essential role, the fluid-vessel system is not a continuum, and the state variable are not continuous function of space because of discontinuities of the state variables. Here the phenomenological or transport coefficients are now function of the fluid and of the vessel [16].

1.2.4 Transport Processes At The Steady State

A process which involves time-dependent parameters is not easy to setup experimentally or to analyze theoretically. The process becomes far simpler to deal with if the state parameters are time independent. This can be achieved when the parameter gradients are externally constrained to constant values. In fact, the empirical transport laws, Fourier's law, etc., were conceived for this case.

Today, as well, most transport experiments are planned so that the state parameters are independent of time. The simplification applies especially to coupled phenomena. It is an experimental fact that, the case of a system with n gradients present, if one gradient is constrained by external

means, all gradients become constant in the course of time. The state that the system eventually reaches is called the *steady or stationary state.* The steady state has considerable theoretical significance. The steady state is the time-invariant ideal state for an open system. It is the counter-part of the time-invariant ideal state for a closed system-*the equilibrium state* [16].

1.3 Mass-Transfer

1.3.1 Modes of Mass Transfer

The movement of material from one location in solution to another, arises from differences in electrical or chemical potential at the two locations, or from movement of a volume element of solution. The modes of mass transfer are:

(1) ***Migration.*** Movement of a charged body under the influence of an electric field (a gradient of electrical potential).

(2) ***Diffusion.*** Movement of a species under the influence of a gradient of chemical potential (a concentration gradient).

(3) Convection. Stirring or hydrodynamic transport.

Generally fluid flow occurs because of natural convection (convection caused by density gradients) and forced convection, and may be characterized by *laminar flow* and *turbulent flow* [17].

1.3.2 Laminar And Turbulent Flow Through Tubes

The flow through tubes can be laminar or turbulent, depending on the magnitude of the dimensionless Reynolds number R_e, which is given by

$$R_e = \frac{\rho v d}{\eta} \qquad (1.9)$$

where v is the fluid velocity (cm/sec), d is the tube diameter (cm), ρ is the fluid density (g/cm^3), and η is the fluid viscosity (poise). Physically the Reynolds number reflects the relative strength of the inertial and viscous forces in the moving fluid. Inertial forces increase with density and with square of velocity (ρv^2). Viscous forces increase with viscosity and velocity and decrease with the increasing tube diameter ($\eta v/d$). The Reynolds number is simply the ratio of these two terms.

At low Reynolds number ($R_e < 2100$) the flow called *laminar* or *viscous*, above this critical Reynolds number *turbulence flow* occurs [18].

1.4 The Diffusion Process

Mass transport on a molecular scale is called *diffusion* and on the scale of the apparatus is termed *bulk motion*, or more precisely, *convection* [18].

Diffusion is a process which leads to an equalization of concentrations within a single phase [4], in which matter is transported from one part of a system to another as a result of random molecular motions ***"random walk"*** [19] , or ***Brownian motion*** [7].

1.4.1 Types of Diffusion Coefficients

Fick studied the interdiffusion of two solutions of the same components but with different concentrations, and also diffusion from a solid into its saturated solution. His diffusion coefficients were therefore ***interdiffusion coefficients*** or ***mutual diffusion coefficients***. In a pure liquid the individual particles move with random motion and have an equal opportunity of taking up any point in the total space occupied by the liquid. If it were possible to label a particle without otherwise changing its properties and to follow its motion through the unlabelled molecules, a ***self diffusion coefficient*** could be defined. Equally, in a multicomponent system, some labelled molecules of component 1 could be introduced so as to form a concentration gradient of labelled and unlabelled species 1 with an otherwise uniform environ-

ment. Application of Fick's law to the interdiffusion of labelled and unlabelled molecules of species 1 gives the *intradiffusion coefficient* of this species within the solution. A self diffusion coefficient is a special case of intradiffusion in a system which contains only the two distinguishable (by isotopic labelling, nuclear magnetic vector orientation, etc.) forms of the same chemical species. An other related experiment comprises adding at some point in space a trace of labelled species 1 to an otherwise homogeneous medium which may, or may not, be multicomponent, and may, or may not, contain unlabelled species 1. Attention is focused on the decay of the initially formed concentration gradient of the labelled species when it is at low concentration in an otherwise homogeneous environment. The resulting diffusion coefficient is termed a *tracer diffusion coefficient*. Also, the orientation of any molecule undergoes random fluctuations and so rotational motion also occurs. This motion ensures that, in the absence of any external field, the molecules do not take up any preferred orientation. When an external field is present the extent of rotational order produced depends upon a balance between the magnitude and direction of the applied field and the intensity of the rotational motion, which in turn depends upon the thermal energy of the system. Removal of the field causes the degree of rotational order which had been induced to decay back to zero at a characteristic rate, then a *rotational diffusion*

coefficient can be defined. All these diffusion coefficients can be related to the translational Brownian motion of the molecules which arises from random fluctuations in the positions of molecules in space as a result of the decay of a concentration gradient, and a ***translational diffusion coefficient*** can be termed for this motion [5].

1.4.2 Basic Hypothesis Of Mathematical Theory

Transfer of heat by conduction is also due to random molecular motion, and there is an obvious analogy between the two processes. This was recognized by Fick, who first put diffusion on a quantitative basis by adopting the mathematical equation of heat conduction derived some years earlier by Fourier. The mathematical theory of diffusion in isotropic substances is therefore based on the hypothesis that the rate of transfer of diffusing substance through unit area of a section is proportional to the concentration gradient measured normal to the section,

$$F = - D \frac{\partial C}{\partial X} \qquad (1.10)$$

where F if the rate of transfer per unit area of section, C the concentration of diffusing substance, X the space coordinate measured normal to the section, and D is the diffusion coefficient.

In some cases, e.g. diffusion in dilute solutions, D can reasonably be taken as constant, while in other, e.g. diffusion in high polymers, it depends very markedly on concentration. If F, the amount of material diffusing, and C the concentration, are both expressed in terms of the same unit of quantity, e.g. grams or grams molecules, then it is clear from Eq. (1.10) that D is independent of this unit and has dimensions ($length^2$ $time^{-1}$), e.g. $cm^2.sec^{-1}$. The negative sign in Eq.(1.10) arises because diffusion occurs in the direction opposite to that of increasing concentration.

It must be emphasized that the statement expressed mathematically by Eq. (1.10) is in general consistent only for an isotropic medium, whose structure and diffusion properties in the neighborhood of any point are the same relative to all directions. Because of this symmetry, the flow of diffusing substance at any point is along the normal to the surface of constant concentration through the point. This need not be true in an anisotropic medium for which the diffusion properties depend on the direction in which they are measured [19].

1.5 Differential Equation of Diffusion

The fundamental differential equation of diffusion in an isotropic medium is derived from Eq.(1.10) as follows. Consider an element of volume in the form of a rectangular parallelepiped whose sides are parallel to the axes of coordinates and are of lengths $2dx$, $2dy$, $2dz$. Let the center of the element be at $P(x,y,z)$, where the concentration of diffusion substance is c. Let ABCD and A'B'C'D' be the faces perpendicular to the axes of X as in Fig.(1.3).

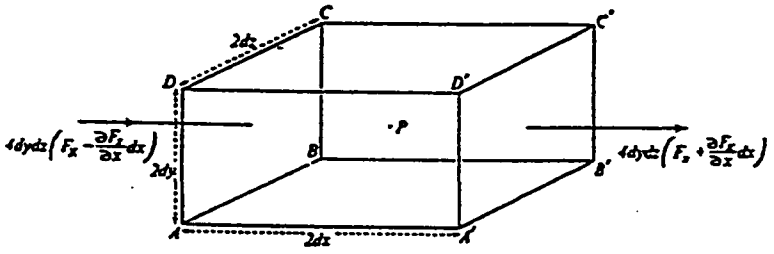

Fig.1.3: Element of Volume

Then the rate at which diffusing substance enters the element through the face ABCD in the plane $(x - dx)$ is given by

$$4\, dydz\, (F_x - \frac{\partial F_x}{\partial x}\, dx)$$

where F_I is the rate of transfer through unit area of the corresponding plane of through P. Similarly the rate of loss of diffusion substance through the face A'B'C'D' is given by

$$4\, dydz\, (F_x + \frac{\partial F_x}{\partial x}\, dx)$$

The contribution to the rate of increase of diffusion substance in the element from these two faces is thus equal to

$$-\, 8\, dxdydz\, \frac{\partial F_x}{\partial x}$$

Similarly from the other faces we obtain

$$-\, 8\, dxdydz\, \frac{\partial F_y}{\partial y} \quad , \quad -\, 8\, dxdydz\, \frac{\partial F_z}{\partial z}$$

But the rate at which the amount of diffusing substance in the element increases is also given by

$$8\, dxdydz\, \frac{\partial C}{\partial t}$$

and hence we have immediately

$$\frac{\partial C}{\partial t} + \frac{\partial F_x}{\partial x} + \frac{\partial F_y}{\partial y} + \frac{\partial F_z}{\partial z} = 0 \qquad (1.11)$$

If the diffusion coefficient is constant, F_x ,F_y ,F_z are given by Eq.(1.10), and Eq.(1.11) becomes

$$\frac{\partial C}{\partial t} = D\,(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2}) \qquad (1.12)$$

reducing simply to

$$\frac{\partial C}{\partial t} = D\,\frac{\partial^2 C}{\partial^2 x^2} \qquad (1.13)$$

if diffusion is one dimensional, i.e. if there is a gradient of concentration only along the X-axis, expressions of Eqs.(1.10 & 1.13) are usually referred to as Fick's first and second laws of diffusion [19,20].

1.6 Solution Methods of the Diffusion Equation when the Diffusion Coefficient is Constant

General solution of the diffusion equation can be obtained for a variety of initial and boundary conditions provided the diffusion coefficient is constant. Such a solution usually has one of two standard forms. Either it is comprised of a series of error function or related integrals, in which case it is most suitable for numerical evaluation at small times, i.e. in the early stages of diffusion, or it is the form of a trigonometrical series which converges most satisfactorily for large values of time. Another solution used the Laplace transform, is essentially an operator method by which both types of solution may be obtained. It is the most powerful of the three, particularly for more complicated problems [19].

1.6.1 Method of Separation of Variables [19,20,21,22,23]

A standard method of obtaining a solution of a partial differential equation is to assume that the variables are separable. Thus we may attempt to find a solution of Eq. (1.13) by putting

$$C(x,t) = F(x) \cdot f(t) \qquad (1.14)$$

where $F(x)$ and $f(t)$ are function of x and t respectively . Therefore

$$\frac{\partial C}{\partial t} = F(x) \cdot f'(t)$$

$$\frac{\partial C}{\partial x} = F'(x) \cdot f(t) \qquad \text{(1.14 a)}$$

$$\frac{\partial^2 C}{\partial x^2} = F''(x) \cdot f(t)$$

substitution of Eq.(1.14 a) into Eq.(1.13) gives

$$F(x)\ f'(t) = D\ F''(x) \cdot f(t) \qquad \text{(1.14 b)}$$

By separation of variables of Eq.(1.14 b) we get

$$\frac{f'(t)}{D\ f(t)} = \frac{F''(x)}{F(x)} \qquad \text{(1.14 c)}$$

Since the left and right sides of Eq.(1.14 c) are respectively function of t only and x only, the equation can be satisfied if each side is separately equal to the same constant, let it be $(-k^2)$, and then we have two equations

$$F''(x) = -k^2\ F(x) \qquad \text{(1.14 d)}$$

and

$$f' = -k^2 D f(t) \qquad (1.14\ e)$$

In the capillary tube diffusion method, which will be discuss in the next chapter, the initial and boundary conditions for a tube close at (x = 0) and open at (x = a) are

$$At\ t=0\ ,\ c=c_o\ \ for\ \ 0<x<a\ \ ,\ c=0\ \ for\ \ x>a$$

$$At\ t>0\ ,\ c=0\ \ at\ \ x=a\ \ and\ \ \frac{\partial c}{\partial x}=0\ \ at\ \ x=0$$

To solve Eq.(1.14 d),

$$F''(x) + k^2 F(x) = 0 \qquad (1.14\ f)$$

the auxiliary equation for a second order linear differential equation is $m^2 + k^2 = 0$. Solving for m we get two complex roots $m = \pm ik$. Then the general solution for Eq. (1.14 f) has the form

$$F(x) = d_1 \cos kx + d_2 \sin kx \qquad (1.14\ g)$$

To find d_1, d_2, and k we use the initial and boundary conditions,

$$F' = (d_1 \sin kx)(-k) + kd_2 \cos kx \qquad (1.14\ h)$$

but we know that at $x = 0$, $F'(x)=0$ so that $F'(0) = kd_2 = 0$. Therefore $d_2 = 0$, and

$$F(x) = d_1 \cos kx \qquad (1.14\ i)$$

We also have at $x = a$, $F(a) = 0$, therefore $F(a) = d_1 \cos ka = 0$, but $d_1 \neq 0$ (if so $F(x) = 0$). Then $\cos ka = 0$, and solving for ka with respect to π at which the $\cos$ function equal to zero we get

$$ka = \frac{2n+1}{2}\pi,$$

$$k = \frac{2n+1}{2a}\pi, \qquad n=0,1,2,... \qquad (1.14\ j)$$

Then $F(x)$ becomes

$$F_n(x) = d_1 \sum_{n=0}^{\infty} \cos\frac{\pi(2n+1)}{2a}x \qquad (1.14\ k)$$

To solve the second equation, Eq. (1.14 e),

$$\frac{f'(t)}{f(t)} = -k^2 D$$

by integration

$$(\ln f(t))' = (- k^2 D t + c_1)'$$
$$\ln f(t) = - k^2 D t + c_1$$

we get for the function $f(t)$,

$$f(t) = c_1 \exp(- k^2 D t) \qquad (1.14\ l)$$

Substituting Eqs. (1.14 k & 1.14 l) into Eq. (1.14) we get

$$C_n(x,t) = \sum_{n=0}^{\infty} B_n \ EXP(-k^2 D t) \ \cos kx \qquad (1.14\ m)$$

where $B_n = c_1 d_1$. To find it's value we use the condition $c(x,0) = 0$ at $x > a$ and $c(x,0) = c_0$ at $0 < x < a$ putting the value of k from Eq.(1.14 j), Eq.(1.14 m) will be

$$c(x,0) = \sum_{n=0}^{\infty} B_n \cos \frac{\pi(2n+1)}{2a} x \qquad (1.14\ n)$$

which can be solved by Fourier analysis as

$$B_n = \frac{2}{a}\int_0^a C_o \cos\frac{\pi(2n+1)}{2a}x \quad dx \qquad (1.14\ o)$$

Upon integrating we obtain

$$\begin{aligned} B_n &= \frac{4C_0}{\pi(2n+1)}\sin[\frac{\pi(2n+1)}{2}] \\ &= \frac{4C_0}{\pi(2n+1)}\ (-1)^n \end{aligned} \qquad (1.14\ p)$$

Substitution of B_n and k in Eq. (1.14 m) yields

$$C(x,t) = \sum_{n=0}^{\infty} \frac{4C_0(-1)^n}{\pi(2n+1)} EXP[\frac{-\pi^2(2n+1)^2Dt}{4a^2}]\cos\frac{\pi(2n+1)}{2a}x \qquad (1.14\ q)$$

By integration of Eq. (1.14 q) in the limit of $0 < x < a$ to get the total concentration at any time t we get the final result

$$C(x,t) = \frac{8aC_0}{x}\sum_{n=0}^{\infty} \frac{(-1)^n}{\pi^2(2n+1)^2} EXP[\frac{-\pi^2(2n+1)^2Dt}{4a^2}]\sin\frac{\pi(2n+1)x}{2a} \qquad (1.15)$$

From Beer's law one can relate the concentration(c) to the absorption of electromagnetic radiation by a compound and to the intensity(I) of the spectrum, so $c(x,t)$ will be equal to $I(t)$ (the intensity of the spectrum at any time), and c_0 will be equal to the I_0 (the initial intensity of the spectrum or the reference one).

In Eq. (1.15), we can replace the ratio of x/a in which x is the total length of the capillary tube (ℓ_t) or the maximum distance that the molecules can go, a is the small length of the tube (ℓ_s) that is under study. Because of the uncertainty in the length of (ℓ_s) which is under the electromagnetic radiation, a ratio R ($R = \ell_s / \ell_t$) can be substituted in the equation, we can rewrite Eq. (1.15) as

$$\frac{I(t)}{I(0)} = \frac{8}{\pi^2 R} \sum_{n=0}^{\infty} (-1)^n f_n(t) \sin \left[\frac{(2n+1)\pi R}{2}\right]$$

where (1.16)

$$f_n(t) = \frac{1}{(2n+1)^2} \exp\left\{\frac{-(2n+1)^2\pi^2 Dt}{4\ell_t^2}\right\}$$

A computer program for Eq. (1.16) has been written and it is listed in Appendix 1.

C H A P T E R T W O

A P P A R A T U S

CHAPTER # 2

APPARATUS

2.1 Introduction

Electron Spin Resonance spectroscopy (ESR), also called Electron Paramagnetic Resonance spectroscopy (EPR), discovered by Zavoisky in 1944, has become an essential tool for the study of the structure and dynamics of molecular systems containing one or more unpaired electrons [24].

2.1.1 Systems Studied by ESR

A large number of systems have been studied by ESR:

(1) Biological system : hemoglobin, nucleic acid, enzymes.
(2) Chemical system : polymers, catalysts, free radicals.
(3) Conduction electrons : alkali and alkali earth metals.
(4) Stable free radicals : in solid and solution, biradicals triplet states.
(5) Gases : NO , NO_2 , SO_2.
(6) Irradiated substances : ionic crystals solid and liquid.
(7) Naturally occurring substance : petroleum, rubber, dolomite, coal.
(8) Semiconductors : doped semiconductors.
(9) Transition elements : single crystals, chelates, sandwich compound, alloys [25].

2.1.2 The Resonance Condition in ESR

Electron is a charged particle with angular momentum (orbital and spin) that possesses a magnetic moment, μ_e, given by

$$\mu_e = - g \beta J \qquad (2.1)$$

Here, J is the total angular momentum vector in units of $\hbar$ where $\hbar$ is the Planck's constant, g is a dimensionless constant (the g-value, g factor, or spectroscopic splitting factor), and β is a constant called the Bohr magneton. The negative sign in the equation is a consequence of negative electronic charge.

Neglecting orbital angular momentum and considering only the total spin angular momentum, S, Eq.(2.1) can be written as

$$\mu_e = - g \beta S \qquad (2.2)$$

The g-value for the free electron, g_e, is 2.0023 for an unpaired electron in an organic molecule or ion, g is generally within a few percent of this value.

The approximation made in Eq.(2.2) is valid for most discussions of the ESR spectra of the organic free radicals and transition metal complexes whose orbital angular momentum can be considered to be "quenched". Treating the g-value as an experimental quantity does not harm the present discussions, since deviations of the g-value from g_e can be accounted for by introduction of spin-orbital coupling.

Magnetic moments can be detected by their interactions with magnetic fields. In zero field, the magnetic moments of unpaired electrons in a sample are randomly oriented. In the presence of a magnetic field H, electron moments assume orientations with respect to the applied field, giving rise to $(2S+1)$ energy states (Zeeman splitting). The measurable components of μ_e are $(g\beta m_S)$, where m_S is the magnetic spin quantum number, which can take the values

$$+S \ , \ +(S-1) \ , \ . \ . \ . \ , \ -(S-1) \ , \ -S \quad .$$

The application of a magnetic field to an $S = 1/2$ (or larger) system is said to remove the spin degeneracy (i.e., the equal energy values of m_S in the absence of an applied magnetic field).

The energy of an electron moment in a magnetic field is given by

$$E = - \mu_e \cdot H \qquad (2.3)$$

Combining eqs.(2.2 & 2.3), the expression

$$E = g \beta H m_s \qquad (2.4)$$

results, assuming the direction of the applied field defines the Z-axis. When $S = \frac{1}{2}$ there are two energy levels , whose energy is linearly dependent on H. The separation between these energy levels (Fig. 2.1) at a particular value of the magnetic field, H_R, is

$$\Delta E = g \beta H_R \qquad (2.5)$$

In an ESR experiment, an oscillating magnetic field perpendicular to H_R induces transitions between the $m_S = 1/2$ and $m_S = -1/2$ levels, provided the frequency, υ, is such that the resonance condition

$$\Delta E = h \nu = g \beta H_R \qquad (2.6)$$

is satisfied. In ESR the frequency is held constant and the magnetic field is varied. At a particular value of the magnetic field, H_R, resonance absorption of energy occurs, resulting in a peak in the spectrum (Fig. 2.1). The frequencies commonly employed in ESR experiments are in the microwave region, these frequencies and magnetic field strengths for g_e resonance absorption signals are given in Table 2.1.

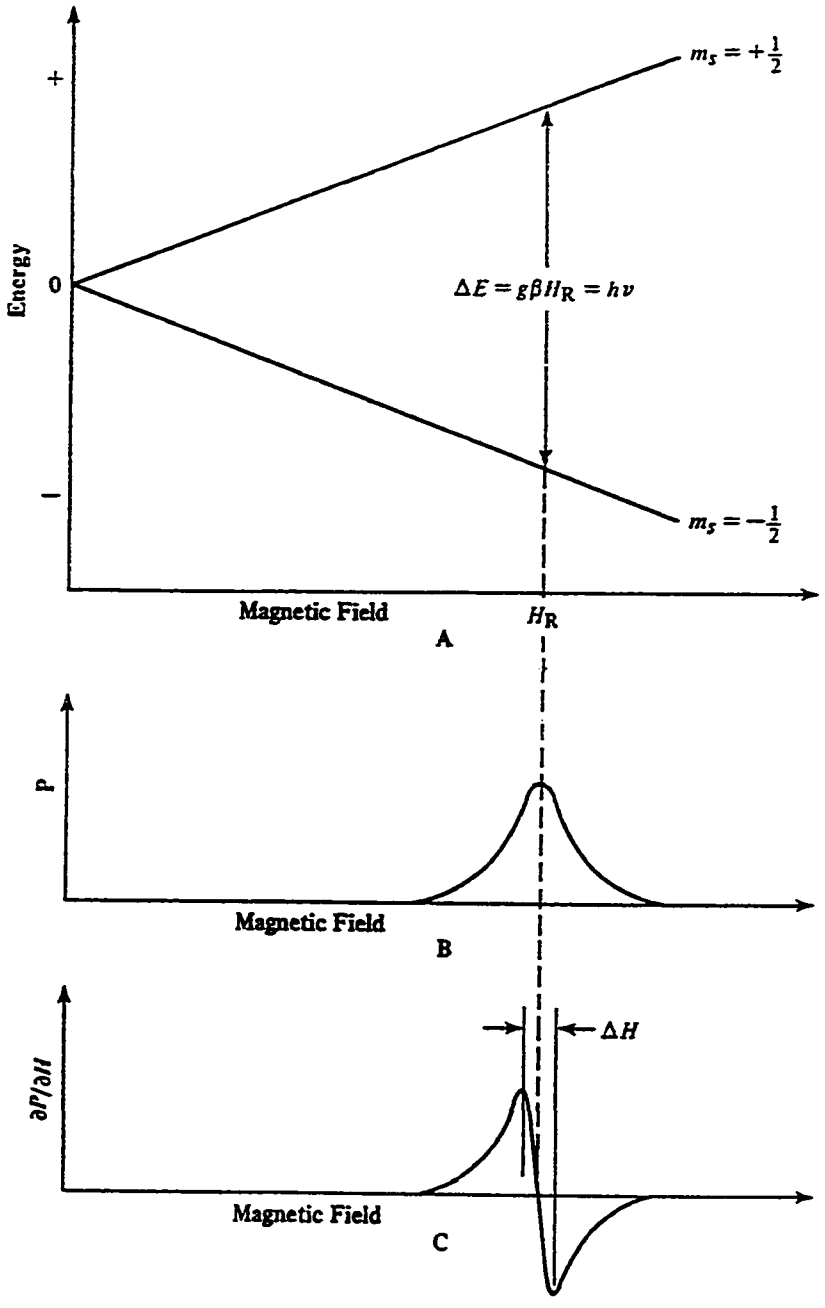

Fig. 2.1 Energy levels and spectra in ESR

Table 2.1 Spectrometer Frequencies and g_e Resonance Field

Designation	υ(Hz)	λ(cm)	$\upsilon(cm^{-1})$	g_e(gauss)
X-band	$\sim 9.5 \times 10^9$	3.156	0.317	3,390
K-band	$\sim 23 \times 10^9$	1.303	0.767	8,207
Q-band	$\sim 35 \times 10^9$	0.856	1.168	12,489

2.1.3 ESR Instrumentation

The instrumentation used in ESR spectroscopy consists of a source of electromagnetic radiation, a sample holder, and appropriate detection equipment for monitoring the amount of radiation absorbed by the sample. In ESR spectroscopy, a magnetic field provided by an electromagnet is also required. Monochromatic radiation of the various frequencies used in ESR work (Table 2.1) is obtained from *klystrons*, which are electronic oscillators producing microwave energy. Spectrometers operating at X-band (3-cm wavelength) are the ones most commonly employed. The microwave radiation is transmitted along hollow rectangular metal pipes called *waveguides*.

Figure 2.2 gives a block diagram of a simple ESR spectrometer. The sample is placed at the center of the cavity, where the magnetic vector is at a maximum. Quartz tubes (approx. 3mm o.d.) are generally used to contain solid and solution samples. Unlike the NMR technique, the sample tubes are not rotated. The magnetic field is slowly and linearly increased until the resonance condition [Eq.(2.6)] is satisfied, at which point power is absorbed by the sample and a change in current in the detector crystal is monitored. A pair of Helmholtz coils is mounted around the cavity to increase sensitivity. Feeding the coils from an oscillator superimposes a variable amplitude sinusoidal modulation on the slowly varying magnetic field.

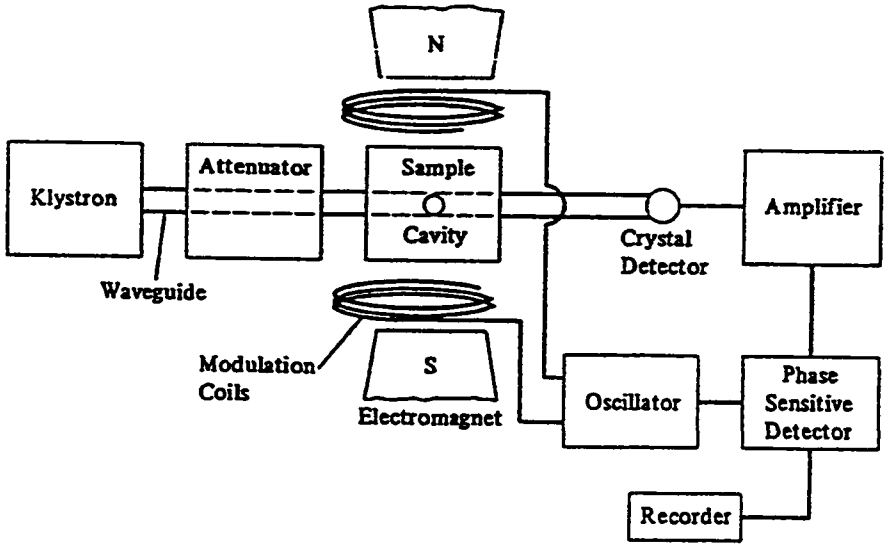

Fig. 2.2 Block diagram of a simple ESR spectrometer

The signal detected by the phase-sensitive detection system is proportional to the slope of the ESR absorption as the magnetic field passes through resonance. The recorder then presents the first-derivative spectrum. Many spectrometers are also equipped to present second-derivative spectra.

The spectral sensitivity of ESR depends on a variety of factors, but with a response time of 1 sec, as few as 10^{11} spins (approx. 10^{-12} moles) can be detected with currently available spectrometers. This sort of sensitivity suggests that ESR spectroscopy would be useful for trace analysis. A minimum detectable concentration is perhaps 10^{-9} *M* is more reasonable, where for qualitative measurement in aqueous solutions, 10^{-7} *M* is more reasonable, where for quantitative measurements the sample concentration should be greater than about 10^{-6} *M*. Concentrations greater than about 10^{-4} *M* should not be used in order to avoid spin-spin (exchange) broadening. For high-resolution studies, dissolved oxygen should be removed because it is paramagnetic and can contribute to line broadening.

In any ESR experiment, it is important to monitor the microwave frequency at which the spectrometer operates and the magnetic-field range swept during the experiment. Although the frequency is constant during an experiment, the frequency available from a given klystron will vary a little with tuning of the instrument. The frequency can be determined using a built-in frequency counters.

The magnetic field can be monitored using an NMR gaussmeter or by using samples of known g-value, for instance, the DPPH free radical, for which $g = 2.0036$. The magnetic sweep can also be checked using Fremy's radical or oxobis(2,4-pentanedionato)vanadium(IV) [24]. More theoretical and experimental details are given in [25,26,27,28,29].

2.2 VARIAN E-109 ESR SPECTROMETER

2.2.1 General Description

The individual units of the E-109 spectrometer are: An electronic (operator's) console, a microwave bridge, a sample cavity with connecting waveguide, a magnet, and a magnet power supply. The system is completely solid state in design with the exception of reflux klystron tube in the microwave bridge and the cathode ray tube in the oscilloscope. The basic electronic console contains the following modules and assemblies:

(1) The E-203B Magnetic Field Controller provides direct control and regulation of the magnetic field in the magnetic air gap.

(2) The E-207 High Frequency Module provides magnetic field modulation frequencies of 25 kHz 100 kHz.

(3) The E-200 oscilloscope displays the ESR signals for visual observation and the klystron power mode for spectrometer tuning.

(4) The E-080B digital drive recorder graphically displays the ESR spectrum as a function of magnetic field or time. The E-102 microwave bridge provides controlled 9.5 GHz microwave frequency to the cavity and detection of ESR signals. The absorption reference arm design permits operation at microwave power levels to one μW. The E-231 series sample cavity is a multipurpose rectangular cavity with an 11 mm sample access. The cavity is designed to permit up to 40 G peak-to-peak field modulation at the sample.

The magnet used is 9-inch in size with the magnet power supply providing the d.c. power to the magnet. The magnet and microwave bridge are water cooled the chilled water supplied by a mechanically refrigerated closed circuit water chiller.

To measure the field value up to 6 significant figures a Varian E-500 NMR gauss meter is used. Similarly, to get the accurate value of the frequency, HP model 5342A microwave frequency counter is used.

2.2.2 Data Acquisition

2.2.2.1 Introduction

The E-935 Data Acquisition system consists of the following four units:

(1) HP 9835 computer

(2) E-935 Data Acquisition System

(3) HP 1350 Graphics Translator

(4) HP 1311A CRT Display

With the use of this computer, one can store the experimental data on a cartridge and later retrieve the data for various analyses, like plotting, manipulation of data, and calculations like g-factor, etc. The data collection becomes fast and efficient with the use of computer.

2.2.2.2 E-935 System Software

The software (provided by Varian Instrument Co.) is divided into four functional modules. Only one of these modules can be present in the memory of the HP 9835 computer at a time. The four functions are: calculation, manipulations, plotting, and scanning.

2.2.2.3 Magnet Scan

ESR data may be acquired while the larger magnet is swept. Magnet scan acquires ESR spectra containing 512, 1024, 2048 or 4096 data points, performs multiscan averaging, and continuously displays the current results on the display unit. Scan time may be in the range of 4-17,000 seconds.

2.2.2.4 Data File Capability

An ESR spectrum may be stored as a data file on a tape cartridge along with a file header containing descriptions of the sample. Experiment and the instrumental settings like field, frequency, power, modulation frequency modulation amplitude, number of scans, scan time, time constant, microwave power, etc. are stored in the file.

Such a data file may be retrieved from a tape cartridge, loaded into computer memory, and subsequently displayed on the display unit. Additional operations can be done on the display with the manipulation module. Also a printed catalogue of the files on a given tape cartridge may be obtained. The displayed spectrum can be immediately plotted.

2.2.2.5 Data Manipulation

With the help of the manipulation module , the following manipulations of ESR spectra may be performed using the interactive capabilities of the display unit and key board:

(1) Base line adjustment of a spectrum.
(2) Combination of two spectra.
(3) Detection of erroneous feature from a spectrum.
(4) Differentiation of a spectrum.
(5) Digital filtration of a spectrum.
(6) Double integration of a spectrum.
(7) X , Y axes scale and shift modifications.
(8) Editing of the file header and recording the spectrum after editing.

2.2.2.6 Tape Cartridge and File System

The tape cartridge serves two main purposes. First, the system tape cartridge contains all of the programs required for proper system operation. The second purpose is to provide for long or short term off-line storage of ESR data sets.

Before use, all tapes must be initialized as per given procedures. An initialized tape is divided into a total of

852 records of 256 bytes per record. There are two tracks per tape. Records 0-425 on the first track, while records 426-851 are on the second track. All information stored on a tape is saved in form of files. All data are contained in a particular file name. To retrieve any data later, a file name must be read to the computer.

2.3 VACUUM SYSTEM

For meaningful ESR line width studies, the sample should be evacuated in order to get rid of oxygen present in the air which is paramagnetic and can interfere with the line width measurements from the paramagnetic sample of interest.

A normal system manufactured by Pope Scientific Inc. was used with slight modification to suit our needs. One of the modifications is a Quick Fit arrangement to insert and remove the sample easily. Also, to measure the vacuum readily, we used a digital vacuum gauge manufactured by Granville-Phillips. Vacuum could be easily reached as low as 1 mTorr and most of the samples were sealed when the vacuum was of that order.

2.4 Capillary Diffusion Apparatus

This technique first introduced by Anderson and Saddington to study the diffusion of ions in solution by radioactive isotopes [30], the capillary cell is charged with the active solution and immersed in the inactive liquid for a known length of time so that normal diffusion can take place. The cell contents are then transferred to a suitable tray, evaporated to dryness, and the radioactive content measured in standard counting equipment. A reference tray is similarly prepared, a known volume of the active solution which has not undergone the diffusion process being used. The activity of this tray is measured immediately after that of the experimental tray, and from the values so obtained, that fraction of the original cell content which has passed out of it as a result of diffusion can be calculated. Knowing the length of the capillary cell and time of diffusion, the self diffusion coefficient of the ion may be calculated [30]. This method has been extensively used for determining self-and tracer diffusion coefficients of electrolytes [31,32,33]. Other studies on theoretical, concentration gradients effect, stirring rate effect, and temperatures effect have been done on this technique [34,35,36,37,38]. This method is shown to be reliable for ESR study, since it reproduces the values of diffusion coefficients that have been reported by other technique [3,9].

To use the capillary diffusion method with ESR spectrometer, a diffusion cell that can be used under solvent vapor pressure is shown in Fig. 2.3. The capillary diffusion cell was made of 1 mm i.d. heavy wall Pyrex tubing whose open end was ground flat. A small distortion of the capillary is unavoidable in joining the capillary to the 11 mm o.d. tubing (A). The total length of the capillary, ℓ_t, was measured with a micrometer. The arm (D) was used to introduce a solid sample to the reservoir (C). Solvent was vacuum distilled into reservoirs (C) and (B) through the O-ring joint (E). The sample preparation and the experimental procedure will be described in the next chapter.

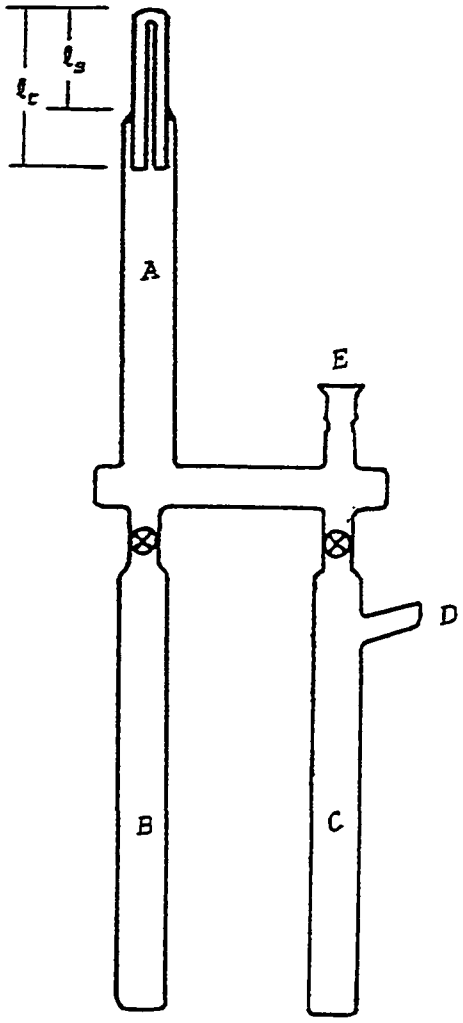

Fig. 2.3 A Capillary Diffusion Apparatus

CHAPTER THREE

PROCEDURE

CHAPTER 3

PROCEDURE

3.1 SAMPLE PREPARATION

3.1.1 VO[5-MeO-Sal SB] (Phen)

This compound was obtained through private communications [39]. The synthesis was carried out following the procedure outlined in reference [40]. The solvent used without further purification is methylene chloride, CH_2Cl_2, (spectroscopic grade purchased from Fluka-AG). A weighted amount is introduced to the cell, and under vacuum the solvent is added the volume of the solvent measure from the reservoir (C) in the cell which is a 10 ml graduate cylinder, the concentration is about ($9.7x10^{-3}$ M).

3.1.2 Cp_2VCl_2

This compound is available commercially (PFALTZ & BAUER, INC), the solvent used is the chloroform, $CHCl_3$, (spectroscopic grade purchased from ARISTAR BDH). The preparation is similar to the above compound, the concentration is about ($8.7x10^{-3}$ M).

3.2 Diffusion Cell Preparation

The following steps done to prepare the cell which contains the sample to be used in the ESR spectrometer:

1. Cleaning and drying the cell carefully.
2. Introduction of the weighted sample through the arm (D), then seal (D).
3. Check that all ports stop cock are close in the vacuum line, connect the cell from the O-ring joint to the vacuum line in one port.
4. Prepare the solvent needed (10-15 Ml) in a clean container and connect it to another port in the vacuum line.
5. Switch on the vacuum pump and open the main stop cock of the vacuum line, to let the pressure goes down.
6. Freeze the sample in reservoir (C) and the solvent container by two liquid nitrogen container.
7. Open the stop cock port at the two ports used, and also the stop cock in the cell at (B) and (C).
8. Degassing the cell and the solvent container until a good, low, stable pressure is obtained.
9. Close the main vacuum line stop cock, and the stop cock at (B) in the cell.
10. Remove the liquid nitrogen from the solvent, to start the evaporation of the solvent from the solvent container to condense at the freeze (C) reservoir which contains the sample.

11. One can repeat steps 6,7,8,9,10 to get more solvent in (C) for certain concentration.
12. Close the stop cock at (C) and open the one on (B), then repeat steps 6,7,8,9,10 for (B) , until good amount is collected from the solvent.
13. Close the stop cock at the solvent port, freeze (B) and (c), then open the stop cock at (B), (C), and the main vacuum line stop cock to remove the vapor of the solvent in the system.
14. Seal below the O-ring joint carefully, then close the two stop cock at (B) and (C) .
15. Close the main stop cock of, switch off the vacuum pump, and release the vacuum system slowly from any unused port to equalize the pressure.
16. Leave the cell to come to room temperature, then check the cell slowly to dissolve the sample with the solvent in (C).
17. Handle the cell pointing the capillary downward, then open slowly the stop cock at (C) to transfer the solution into the capillary through (A).
18. If a bubble of the vapor block the solution to inter the capillary, remove it by rubbing the capillary with fingers or small cloth slowly and carefully.
19. The excess liquid is poured back into (c), and the cell gently shaken to disperse any paramagnetic solution coating the wall of (a).

20. Put the cell in the ESR cavity at the close end to set up the parameters for the ESR spectrometer, use collars available to set the length of the capillary in the cavity and fix it to the cell by tape.
21. Maximum lines height should be obtained from the ESR parameter setting because these lines will decrease by time, so by the end of the experiment it will be readable.
22. Remove the cell from the cavity, open the stop cock at (B) slowly to transfer the solvent above the capillary cell in (A), put back the cell in the cavity, record the time, and take the first spectrum run.
23. The cell should not disturb in the cavity, three to four runs should be taken every day, with the same setting of the ESR spectrum parameter. Each run record the time and find the difference of time of this run and the time when the experiment start in seconds.
24. Analyze the spectrum of each run by finding the intensity of each line by the computer manipulation program, the first run can be taken as a reference, find the total intensity of the reference spectrum, enter these values into a data file for the computer program (in the appendix the program and the data files are listed for the two compounds) called Diff.
25. The data are collected for three to four weeks.

26. Run the program at the end will give two output files one to calculate the diffusion coefficient, and the other you can plot the total intensity as a function of time from the output file plot generated.

3.3 ESR Spectrometer Operation

The following is a brief description of how to operate the ESR spectrometer:

(i). Put on the chiller water for circulation .

(ii). Turn the console power on and bring the field set slowly to the central field value (≈ 3300 - 3400 G), through the zero value.

(iii). In the microwave bridge the STANDBY setting to TUNE position, while keeping the microwave power around 40 Db.

(iv). Adjust the iris and turn on the frequency counter.

To record the spectra the capillary must be at the active region of the cavity, this could be adjusted with the collars provided. Proper tuning procedure should be followed on the microwave bridge.

Keep the field set at 3300 G, scan range of 1000 G for the room temperature spectra. For good line shape analysis, the spectra taken must be free from artifact broadening due to the wrong selection of spectrometer parameters like scan speed,

time constant, microwave power, modulation amplitude, etc. To get the right signal, first increase the modulation amplitude until no peak no peak distortion or line width increase is noticed. This value of modulation amplitude could be used for the experiments subsequently. Second, increase the microwave power until the saturation of the peak occurs. Once the right spectra are plotted, then they are stored to the tape for Varian Spectrometer, and plotted also by the plotter, the ESR parameters for the compounds are tabulated in Table 3.1.

Table 3.1 The ESR Parameters For Experiments

Parameters	Compound I	Compound II
Number of Point	2048	2048
Number of Scans	4	1
Field Set (G)	3440.73	3410.00
Scan Range (G)	1000	800
Scan Time (sec)	120	180
Modulation Frequency (kHz)	100	100
Modulation Amplitude(G)	2	2
Receiver gain	1.25×10^4	4.0×10^4
DC Gain	Normal	Normal
Time Constant	0.25 s	0.25 s
Microwave Power	2 mW	20 mW
Microwave Frequency (GHz)	9.489787	9.51050

Compound I : VO[5-MeO-Sal SB] (Phen)

Compound II : Cp_2VCl_2

CHAPTER FOUR

ESR MAGNETIC PARAMETERS

CHAPTER #4

ESR MAGNETIC PARAMETERS

4.1 Introduction

The analysis of the spectra to extract the magnetic parameters of the complex is obtained from the rigid limit and room temperature spectra according to Wilson and Kivelson's method [41]. The parameter are necessary for a proper interpretation of the observed ESR spectra at various temperatures in terms of correlation time τ_1 and anisotropic rotational diffusion (N). The ESR spectra of Cp_2VCl_2 in chloroform ($CHCl_3$) at various temperatures, in the motional narrowing region, is analyzed to study the anisotropy of molecular rotation (N) defined as the ratio $R_\parallel/R_\perp$ where $R_\parallel$ is the rotational diffusion constant along the molecular principal axis of rotation, and $R_\perp$ is the rotational diffusion constant perpendicular to the molecular principal axis of rotation [42,43,44]. The results are compared with the anisotropy of rotation (N) calculated from Stokes-Einstein model [11] and that calculated from the Allowed-Values Equation (AVE) [45]. This comparison demonstrates the applicability of these narrowing motion region equations to experimentally observable system as well as giving some valuable information about the structure. From the analysis of the temperature dependent ESR

line shapes in the motional-narrowing reagin the stickiness factor (S) which is a measure of all non-hard-core interactions is determined [15,46,47]. Also we will show how the dependence of line widths on temperature is utilized to obtain the anisotropic factor (N) and the correlation time τ_R. These experimental N values are compared with theoretical values [11,45].

The vanadyl radical has an electron spin of half (unpaired electron, d^1-system) which interacts with the vanadyl nucleus which has the spin I=7/2 therefore the ESR spectrum consist of (2I+1), that is eight lines.

4.2 Spin Hamiltonian and Definition of the Parameters

The appropriate spin Hamiltonian, H_S, required to describe the vanadyl paramagnetic systems in general is [48,49],

$$H_S = B\,\beta_0\,g.S + S.A.I + \text{(electron-electron dipole term)} + \text{(electron-electron exchange term)} + \text{(nuclear Zeeman term)}$$

The first term is the electron Zeeman term and the second term is the electron-nuclear hyperfine interaction term, where B is the laboratory magnetic field, β_0 is electron Bohr magneton, g the electron g-value tensor, S is the electron spin angular

momentum operator, A is the electron-nuclear hyperfine tensor, and I is the nuclear spin angular momentum operator. The nuclear Zeeman term is not important in most work [50] and will be omitted.

The electron-electron dipole and exchange terms are significant only when very high concentration [51] and single crystals studies [52] are considered, so our Hamiltonian will be,

$$H_s = B\beta_0 g.S + S.A.I \qquad (4.1)$$

4.2.1 ESR Spectra in Solution

The ESR spectra of the vanadyl complexes in liquid solution can be described by the isotropic electron Zeeman and electric-nuclear hyperfine interactions included in the spin Hamiltonian [41,53] as in eq.(4.1), the allowed transitions when microwave field at frequency ω_0 is applied, occur at the field B which satisfies the resonance condition [41,53]

$$\omega_o = g_o\beta_o\frac{B}{h} + A_oM + \frac{1}{2}A_o^2\left[\frac{I(I+1)-M^2}{g_o\beta_o(B/h)}\right] \qquad (4.2)$$

where ω_0 is the microwave frequency in radians per second, h is the Planck's constant divided by 2π, $I = 7/2$, M is the

nuclear spin magnetic moment, B is the resonant value of the magnetic field corresponding to M,

A_0 is the isotropic hyperfine constant in radians per second,

$$A_o = \frac{1}{3} (A_x + A_y + A_z) \tag{4.3}$$

and g_0 is the isotropic g-factor,

$$g_o = \frac{1}{3} (g_x + g_y + g_z) \tag{4.4}$$

where X, Y, and Z refer to the molecule fixed coordinates, and it has been assumed that g and A can be simultaneously diagonalized.

The contact hyperfine constant A_0 can be obtained to second order by taking the difference of B_M for line M and B_{-M} for line $-M$

$$A_o = \frac{g_o \beta_o (B_M - B_{-M})}{2Mh} \tag{4.5}$$

furthermore,

$$g_o - g_s = g_s\left[\frac{B_s - \frac{1}{2}(B_M + B_{-M})}{\frac{1}{2}(B_M + B_{-M})}\right] - \frac{2A_o^2 h^2 [I(I+1) - M^2]}{g_s \beta_o^2 (B_M + M_{-M})^2} \qquad (4.6)$$

where g_S and B_S are the isotropic g-value and the resonant value of the magnetic field (in Gauss), for standard of known g-value. For our system, the standard used is diphenylpicrylhydrazyl (DPPH), with g-value equal to 2.0037.

The first term in eq.(4.1) the electron Zeeman term, represents the large interaction of the electron spin with the laboratory magnetic field. This term yields the relation,

$$h\,\upsilon = g_o\,\beta_o\,B \qquad (4.7)$$

where h is Planck's constant and υ is the microwave frequency of the ESR spectrometer. This equation can be reduced to [26],

$$\upsilon \text{ (in GHz)} = 2.80247\ (g_0 / g_e)\ B \text{ (in kG)} \qquad (4.8)$$

For vanadyl complexes eq.(4.8) can be further reduced to,

$$\upsilon \text{ (in GHz)} = 2.847 \quad B \text{ (in kG)} \qquad (4.9)$$

This relation serves as a useful conversion factor. Most ESR spectrometers operate at υ = 9.5 GHz (X-band), and thus B = 3.3 kG. The unpaired electron responsible for the ESR spectrum is confined largely to the vanadyl center, which interacts with the nuclear spin of ^{51}V (I = 7/2), the result is (2I + 1) or 8 lines separated by a coupling constant with different intensities. This nuclear interaction is represented by the second term in eq.(4.1). It is apparent from the variation in the intensities of the lines that the line widths of the different hyperfine components are not equal and depend on the ^{51}V nuclear spin quantum number [41,53].

This line width variation indicates that the anisotropic hyperfine and Zeeman interaction are not completely average out by the tumbling of the molecules in the liquid, and they contribute significantly to the lines width. The relation of the important A_0 and g_0 parameters are shown in (Fig. 4.1) along with the lines widths (ΔH) and the peak heights (h) in a first derivative representation of the absorption curve. The spectra can be recorded with the opposite phase from that of Fig. 4.1 producing an upside down effect. The presentation most consistent with current trends in spectroscopy involves positive phase and increasing *B* from left to right.

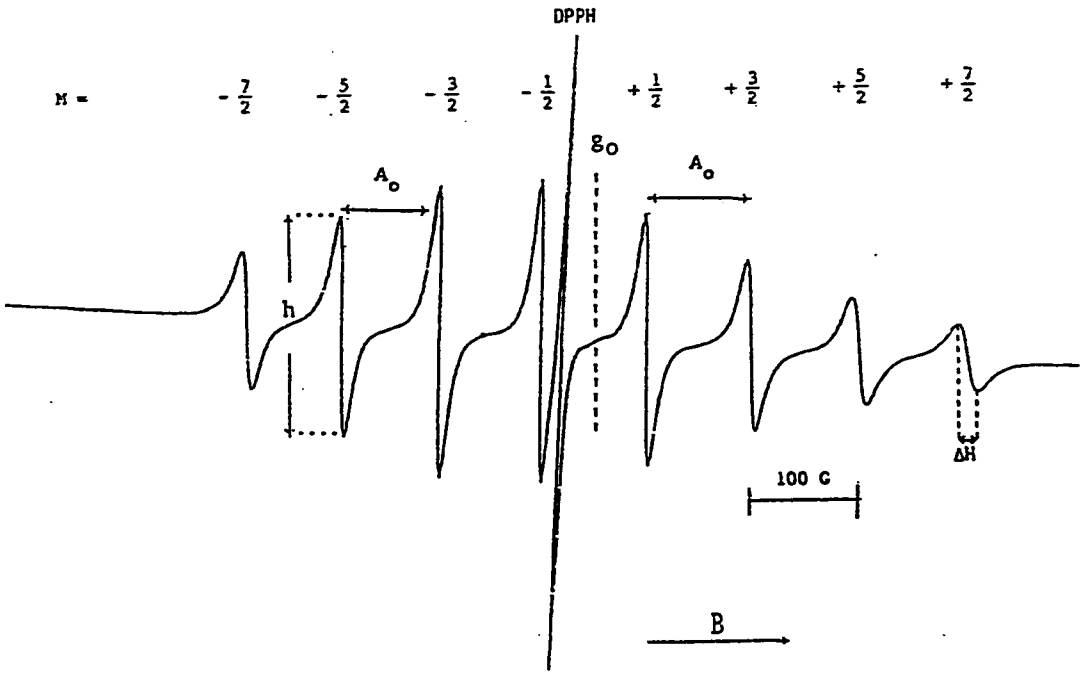

Fig. 4.1: A Typical X-band Spectrum Of Oxovanadium (IV) in Solution at Room Temperature.

4.2.2 ESR Spectra in the Absence of Molecular Motions

4.2.2.1 Anisotropic Effects

The glass spectrum of vanadyl probes can be described in terms of the Zeeman and nuclear-electronic hyperfine interactions by the spin Hamiltonian [41,49,54],

$$H_s=\beta_o(g_xB_xS_x+g_yB_yS_y+g_zB_zS_z)+A_xS_xI_x+A_yS_yI_y+A_zS_zI_z \qquad (4.10)$$

a special case of eq.(4.1), both g and A depend on the orientation of the magnetic field in terms of molecular coordinates and the direction of B. The extremes in g and A lie along the principal X, Y, and Z axes. The glass ESR spectrum of a typical VO^{2+} at (77 k) is illustrated in Fig. 4.2 this glass spectrum of vanadyl complexes is governed by [41],

$$\omega_o=\frac{g\beta_oB_M}{h}+AM+\frac{(A_x^2+A_y^2)(A_z^2+A^2)}{8A^2}\frac{[I(I+1)-M^2]}{g\beta_oB_M/h} \qquad (4.11)$$

where

$$g = (g_x^2 \cos^2\theta + g_x^2 \sin^2\theta \cos^2\varphi + g_y^2 \sin^2\theta \sin^2\varphi)^{\frac{1}{2}}$$

and

$$gA = (A_x^2 g_x^2 \cos^2\theta + A_x^2 g_x^2 \sin^2\theta \cos^2\varphi + A_y^2 g_y^2 \sin^2\theta \sin^2\varphi)^{\frac{1}{2}}$$

θ is the angle between B and unique molecular axes, and φ is the azimuthal angle. Note that the line for which $\theta = 0$ gives rise to the spectrum corresponding to g_z and A_z in (Fig. 4.2) while those for which $\theta = \varphi/2$, $\varphi = 0$ and $\pi/2$ give rise to the "doubled spectra " corresponding to (g_x ,A_x) and (g_y ,A_y) as in Fig. 4.2. The anisotropic tensors can be determined from ridged limit spectra, Fig.4.2, as Wilson and Kivelson have done, for vanadyl acetylacetonate VOAA [41]. The spacings I, II, III, IV, and V in Fig.4.2 correspond to,

$$A_x = \frac{II + III}{2} \qquad (4.12)$$

$$A_x + A_y = IV + V \qquad (4.13)$$

$$I = \frac{\beta_o B 2\delta_g}{h} + 4c\left(\frac{7}{2}\right) \qquad (4.14)$$

where

$$\delta_g = \frac{1}{2} (g_x - g_y) \tag{4.15}$$

$$C = \frac{1}{4} (A_x - A_y) \tag{4.16}$$

although the values of g_X, g_Y, g_Z and A_X, A_Y, A_Z obtained from the glassy spectrum are compatible with the isotropic values obtained from the liquid spectrum, the most accurate determinations of the magnetic parameters are obtained by measuring g_0 and A_0 from the liquid spectrum, g_Z, $g_X - g_Y$, A_Z and $A_X - A_Y$ from the glass spectrum, and g_X, g_Y, and A_X, A_Y from this data and eqs. (4.14 and 4.15) [41].

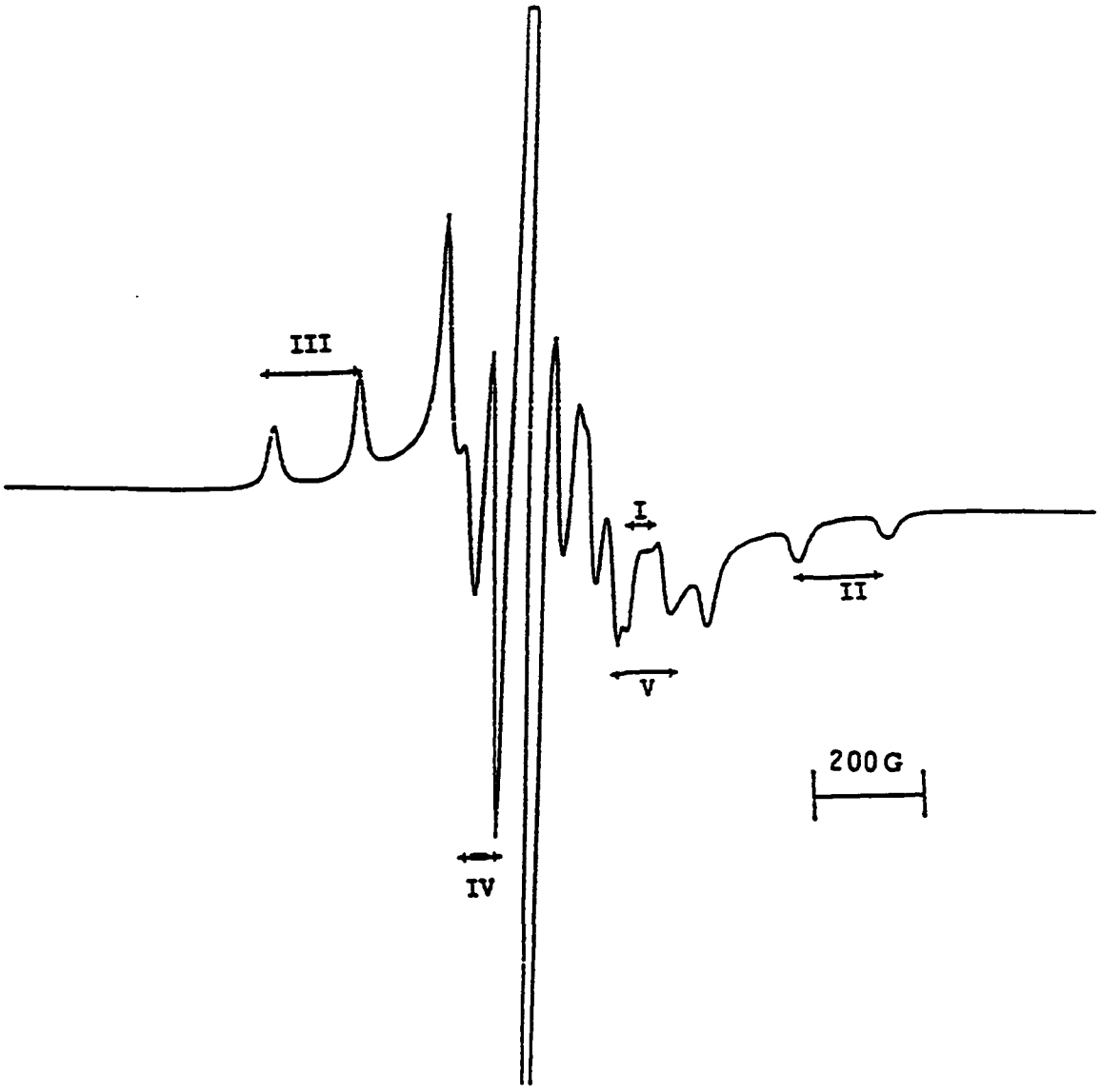

Fig. 4.2 Ridgid Limit spectra at 77 k

4.2.2.2 The Effects of Rotational Motion on ESR Spectra

The shape of an EPR spectrum is markedly dependent upon the rotational mobility of the paramagnetic spin probe. For example, in a nonviscous solvent nearly all vanadyl probes exhibit eight sharp lines. The rapid isotropic tumbling motion averages out all anisotropic effects discussed above, therefore sharp lines are obtained. If the rotational motion is slowed down by increasing the solvent viscosity, averaging is incomplete. The result is unequal broadening of the eight lines. Molecular motion is not necessarily isotropic. Preferential motion about one axis is likely to occur for any asymmetric spin probe, but the effects are particularly evident when surrounding medium is anisotropic. The ESR spectrum is very sensitive to the probe mobility. The best way to make use of this sensitivity is to describe the motion quantitatively in terms of the shape of the spectrum.

As discussed above, both the anisotropic hyperfine electron-nuclear interaction and the anisotropic spin-orbit interaction in a spin probe depend on the mutual orientation of the external magnetic field and of π-orbital of the unpaired electron. Rotations of the probe modulate these interactions, leading to fluctuations in local magnetic fields and changes of the ESR line widths. Rotational motion is characterized by correlation time (τ_R) which determines the effective frequency of rotation, f_{eff} (in Hz) $= (2\pi\tau_R)^{-1}$.

The principal g and A values are related to the isotropic g_0 and A_0 values through eqs (4.3 and 4.4).

The anisotropy of g and A tensors is applied in dynamic spin probe studies to get information about the motional state of the probe. Between the two limits of very rapid motion and a rigid glass, the spectra are quite complex. This complexity provides much of the information that can be obtained about molecular motion using spin probe techniques.

4.3 The Correlation Time Group

The correlation time data of vanadyl complexes usually divided into three groups,

Rapid rotations	10^{-11}	-	10^{-9}	sec.
Slow rotations	10^{-9}	-	10^{-6}	sec.
Very Slow rotations	10^{-6}	-	10^{-3}	sec.

The limits of these regions are essentially determined by the anisotropy of the magnetic interactions occurring in the probes.

4.4 Molecular Tumbling

The spin Hamiltonian can be divided into,

$$H = H_o + H_1(\Omega) + \varepsilon(t) \qquad (4.17)$$

where

$$H_o = \beta_o g_o B S_z + A_o I.S \qquad (4.18)$$

where S_S is the electron spin along the Z-axis, S and I are the electron and the nuclear spin operator, B is the laboratory magnetic field, and β_0 is electron Bohr magneton, and H_1 is equal to,

$$H_1 = \beta_o B.g S + I.A.S \qquad (4.19)$$

where g and A contain the an isotropic components of the electron g-tensor and electron-nuclear dipole hyperfine tensor after the isotropic components g_0 and A_0 have been subtracted. These tensors are defined in terms of molecular fixed axis whose orientation varies with time, with respect to the laboratory magnetic field due to molecular motion.

Thus the time dependence of H_1 is modulated by the reorientational motion of the molecule (Ω), and

$$h\varepsilon(t) = \frac{1}{2} h \gamma_e B[S_+ \exp(-i\omega t) + S_- \exp(i\omega t)] \quad (4.20)$$

where

$$S_+ = S_x + iS_y$$

is the raising operator,

$$S_- = S_x - iS_y$$

is the lowering operator, γ_e is the magnetogyric ratio of a free electron and ω is the microwave frequency. $\varepsilon(t)$ gives the interaction of the spin with the microwave radiation field which must be included in the Hamiltonian if the saturation effects are to be considered. Saturation effects are known to be negligible for experimental spectra discussed, only terms linear in $\varepsilon(t)$ must be considered [54]. The term "fast" and "slow" refers to the randomly fluctuating part $H_1(t)$ spin Hamiltonian (where $H_1(t)$ has a time averaged value zero) in relation to a correlation time τ_R which characterizes the underlying stochastic process.

Fast motional theories are applicable if $|H_1(t)|\tau_R << 1$ where $H_1(T)$ is expressed in frequency units. On the other hand, the slow tumbling is attained when $|H_1(t)|\tau_R >> 1$. Since the slow and the very slow rotations lie outside the scope of this work, only the fast tumbling rotations will be discussed.

4.5 Fast Tumbling

It is convenient at this point to define a line width parameter T_2. If the peak to peak width is ΔH (in gauss), then $1/T_2 = \Delta H$. In general, the dependence of T_2 upon M, the component of the nuclear spin along the direction of the applied magnetic field is given by,

$$T_2^{-1}(M) = A + BM + CM^2 + DM^3 \qquad (4.21)$$

where A, B, C, and D depend on the magnetic tensors. The line width contributions can be calculated with the Redfield relaxation matrix theory as applied by Freed and Fraenkel [55,56] or with the theory of Kubo and Tomita as applied by Kivelson [57].

In order to determine the anisotropy of rotation (N) and the axis of rotation, the motional narrowing analysis of Freed *et al.* [42,43,44] has been used and eq.(5) in reference [44] has been used.

In practice τ_R is obtained from *B*, C,and *D* coefficients because of the uncertainty in *A* [51]. The theoretical expressions for *B* and *C* coefficients will be discussed in the next chapter [42,43].

For isotropic Brownian $\tau_R = (6R)^{-1}$ where R is the rotational diffusion coefficient. For the eight lines spectrum for vanadyl probe, eq.(4.21) will give rise to four experimentally determined unknowns, *A*, *B*, *C*,and *D* . Since the line width coefficients *B* and *C* are function of τ_R values, in the case of two values of τ_R value not agreeing, the assumption of anisotropic rotation must be suspected. Fortunately, this restriction has been resolved by Freed and his co-worker [43,58]. The cubic dependence of $(1/T_2)$ on M given in eq.(4.21) is retained, but the motion is described by a rotational tensor *R*. This is often axially symmetric and is defined by two components $R_\parallel$ and $R_\perp$, where $R_\parallel$ is the rotational diffusion constant along the principal axis of rotation, and $R_\perp$ is the rotation diffusion constant perpendicular to the principal axis of rotation. The anisotropy of rotation (N) is defined as the ratio of $R_\parallel/R_\perp$.

Two related correlation times $\tau(0)$ and $\tau(2)$ are given by,

$$\tau(0) = (6R_\perp)^{-1} \qquad (4.22)$$

$$\tau(2) = (2R_\perp + 4R_\parallel)^{-1} \qquad (4.23)$$

Reference should be made to the original literature [43,58] and more recent work [59] for details of this analysis.

CHAPTER FIVE

RESULTS AND DISCUSSION

CHAPTER # 5

RESULTS AND DISCUSSION

5.1 DETERMINATION OF THE MAGNETIC PARAMETERS

5.1.1 Isotropic Magnetic Parameters

The spectrum of Cp_2VCl_2 is shown in (Fig.5.1). The isotropic hyperfine constants, A_0, and g_0 were obtained from B_M for line M and B_{-M} for line $-M$ by eq.(4.5) and eq.(4.6). A_0 and B_0 were determine for each pair of M and $-M$ lines and average over all pairs.

5.1.2 Anisotropic Magnetic Parameters

The rigid limit of Cp_2VCl_2 is shown in (Fig.5.2). The anisotropic tensors were determined from this rigid limit spectrum using second - order perturbation theory , and from the isotropic A_0 and g_0 determined from the liquid spectra, as Wilson and Kivelson have done for VOAA [41]. Spacings II and III , from the rigid limit spectrum are used in eq.(4.12) to determine A_I

$$A_I \text{ (G)} = (\text{ II } + \text{III })/2$$

as the resonant lines for the magnetic field parallel to Z-axis ($H \parallel Z$) are concentric around g_I value . From the two terminal resonant lines in the glass spectrum, (Fig.5.2), which corresponds to $H \parallel Z$ ($B_{-7/2}$ and $B_{7/2}$) value of g_I can be obtained as follows,

$$g_z = \frac{h\nu}{\beta_o} / \left[\frac{B_{\frac{7}{2}} - B_{\frac{-7}{2}}}{2}\right] \qquad (5.1)$$

where h is Planck's constant, υ is the microwave frequency in Hz, β_0 is the Bohr magneton. combining the values of A_I and g_I obtained from rigid limit spectrum with those of A_0 and g_0 obtained from the liquid spectra in eq.(4.3) and eq.(4.4), values of $A_I + A_J$ and also $g_I + g_J$ were obtained as follows,

$$A_x + A_y = 3A_o - A_z \qquad (5.2)$$

$$g_x + g_y = 3g_o - g_z \qquad (5.3)$$

the rigid limit resonant lines for $H \parallel Z$ are governed by,

$$\omega_o = \frac{g_z \beta_o B_M}{h} + A_z M + \frac{(A_x^2 + A_y^2)\left(\frac{63}{4} - M^2\right)}{4 g_z \beta_o B_M / h} \qquad (5.4)$$

which is the case in eq.(4.11) where $\theta = 0$. Substituting A_Y with respect to A_X from eq.(5.2) in eq.(5.4) will yields A_X value which can be used in eq.(5.2) again to get A_Y . Using eq.(5.4) and resonant lines for $H \parallel Z$, the tensors obtained above were further adjusted. Spacing I is

$$I\ (Hz) = \left[\frac{\beta_o B\ (g_x - g_y)}{h}\right] + \frac{7}{2}\ (A_x - A_y) \qquad (5.5)$$

where B (in gauss) is calculated from the microwave frequency (in Hz) and g_0 by eq.(4.7), spacing I measured from the rigid limit (Fig.5.2) in gauss, should be used in eq.(5.5) in Hz. substituting A_X and A_Y values obtained from eq.(4.5) and values of g_Y from eq.(5.3) the following expression obtained,

$$I\ (Hz) = \left[\frac{\beta_o B\ (2g_x + g_z - 3g_o)}{h}\right] + \frac{7}{2}\ (A_x - A_y) \qquad (5.6)$$

which is solved to give the g_X value and then g_Y is also obtained using eq.(5.3).

Again when $\theta = \pi/2$ and $\varphi = 0$ and $\pi/2$ in eq.(4.11) yield the following two equations which govern the resonant lines for $H \parallel$ X-axis and $H \parallel$ Y-axis respectively,

$$\omega_o = \frac{g_x \beta_o B_M}{h} + A_x M + \frac{(A_x^2 + A_y^2)(A_x^2 + A_z^2)(\frac{63}{4} - M^2)}{8 A_x^2 g_x \beta_o B_M / h} \qquad (5.7)$$

$$\omega_o = \frac{g_y \beta_o B_M}{h} + A_y M + \frac{(A_x^2 + A_y^2)(A_y^2 + A_z^2)(\frac{63}{4} - M^2)}{8 A_y^2 g_y \beta_o B_M / h} \qquad (5.8)$$

The above two equations are used to verify the calculated values of the g and A tensors.

Several magnetic parameter values for Cp_2VCl_2 have been reported [62,65,66,67], these values are tabulated in table 5.1, the experimental result obtained from temperature variation and the line width measurements [13], will be analyzed by using the reported values to find the best reported value, from which we determine the anisotropy of rotation **N** .

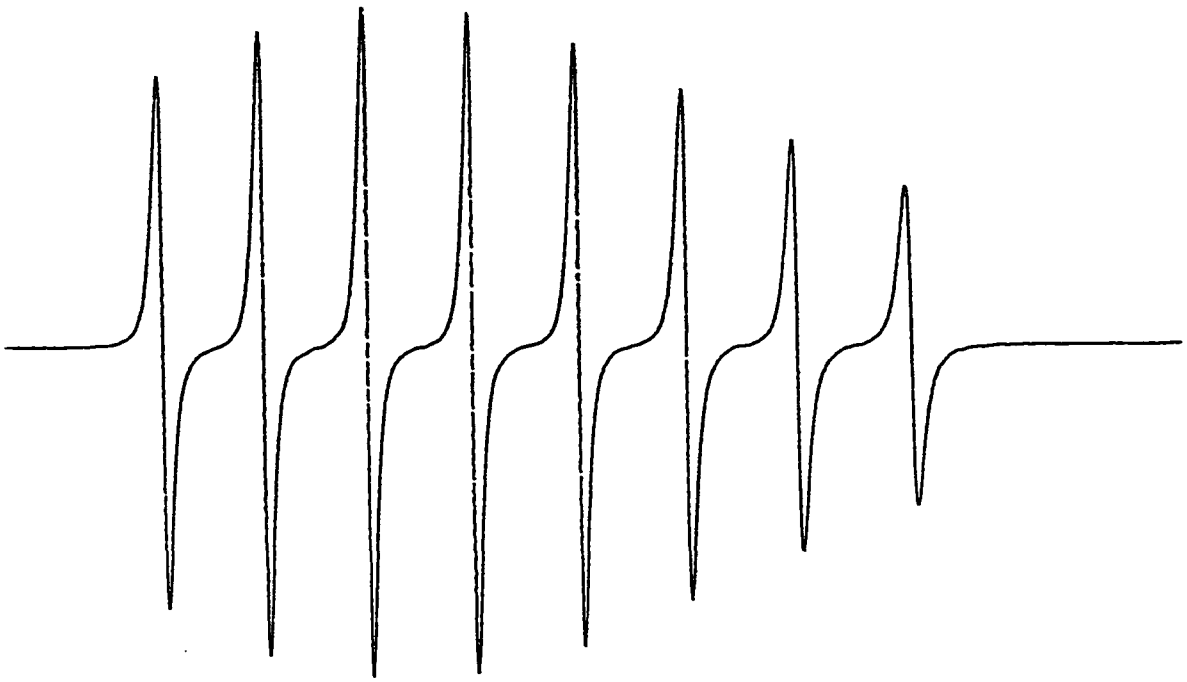

Fig. 5.1: X-band Spectrum of Cp_2VCl_2 at room temperature.

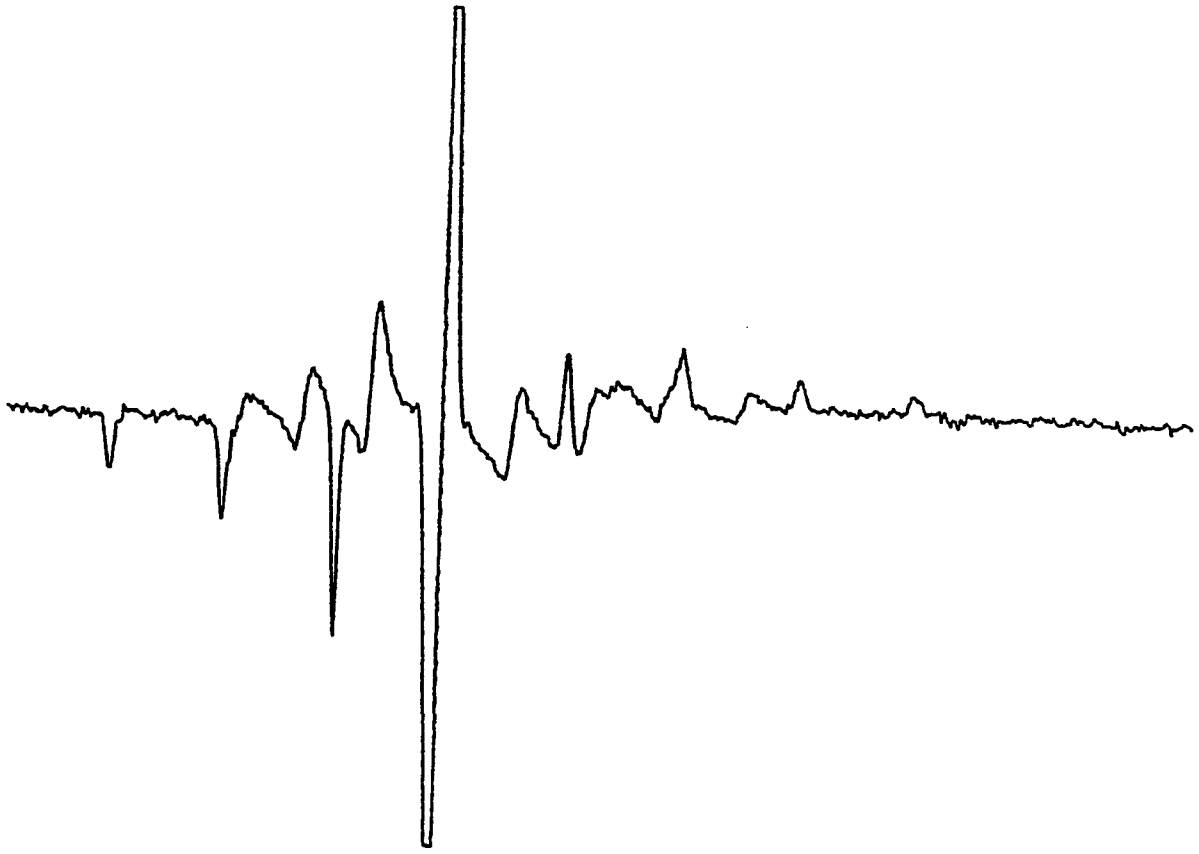

Fig 5.2: X-band Spectrum of Cp_2VCl_2 at T = 77 K.

Table 5.1: Reported Magnetic Parameters for Cp_2VCl_2

Mag.Par in (G)	(a)	(b)	(c)	(d)
g_x	1.986	1.965	1.986	1.9802
g_y	1.971	1.946	1.971	1.9695
g_z	2.000	1.967	2.010	2.0013
g_0	1.98567	1.95933	1.98900	1.98367
A_x	79.808	81.974	76.444	80.600
A_y	126.183	130.065	123.818	125.500
A_z	16.177	29.511	20.457	20.600
A_0	74.05611	79.44862	75.13467	75.56670

(a) C. P. Stewart and A. L. Porte [66], Cp_2VCl_2 in CH_2Cl_2 + toluene.

(b) D. P. Bakalik and R. G. Hayes [67], Cp_2VCl_2 in CH_2Cl_2 + toluene.

(c) A. T. Casey and J. B. Raynor [65], Cp_2VCl_2 in toluene.

(d) J. L. Petersen and L. F. Dahl [62], Single-Crystal EPR Study of $V(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$ Doped in $Ti(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$.

5.2 MOTIONAL NARROWING ANALYSIS

The spectra in Fig. 5.3 are those of Cp_2VCl_2 in toluene taken over a temperature range (294 - 178 K). This free radical has an electron spin (1/2) which interacts with the vanadyl nucleus which has spin I = 7/2 , therefore the ESR spectrum consists of eight lines each corresponding to a nuclear spin magnetic quantum number M:

$$M = I, I-1,\ldots,-I$$

The line width parameter, T_2 (in $gauss^{-1}$) , of each of these lorentzian hyperfine lines can be described by an expansion in M , the component of the nuclear spin along the direction of the applied magnetic field given by eq.(4.21) .

The line widths and the peak to peak heights are obtained experimentally utilizing the computer graphic display which facilitates on screen line width measurements [13]. After measuring the line widths of each of these line, the widths are then entered into the computer program written for eq(4.21) for polynomial regression (called POLREG in Watfive computer language) where the coefficients of the best polynomial fit are output for the experimental values by using least square fitting, since our fitting is cubic four coefficients will be produce A(0)=A, A(1)=B, A(2)=C, and A(3)=D . The B and C values for different temperatures are shown in (Table 5.2) with the lines widths, also (Fig.5.4) shows the B Vs C plot of the experimental values.

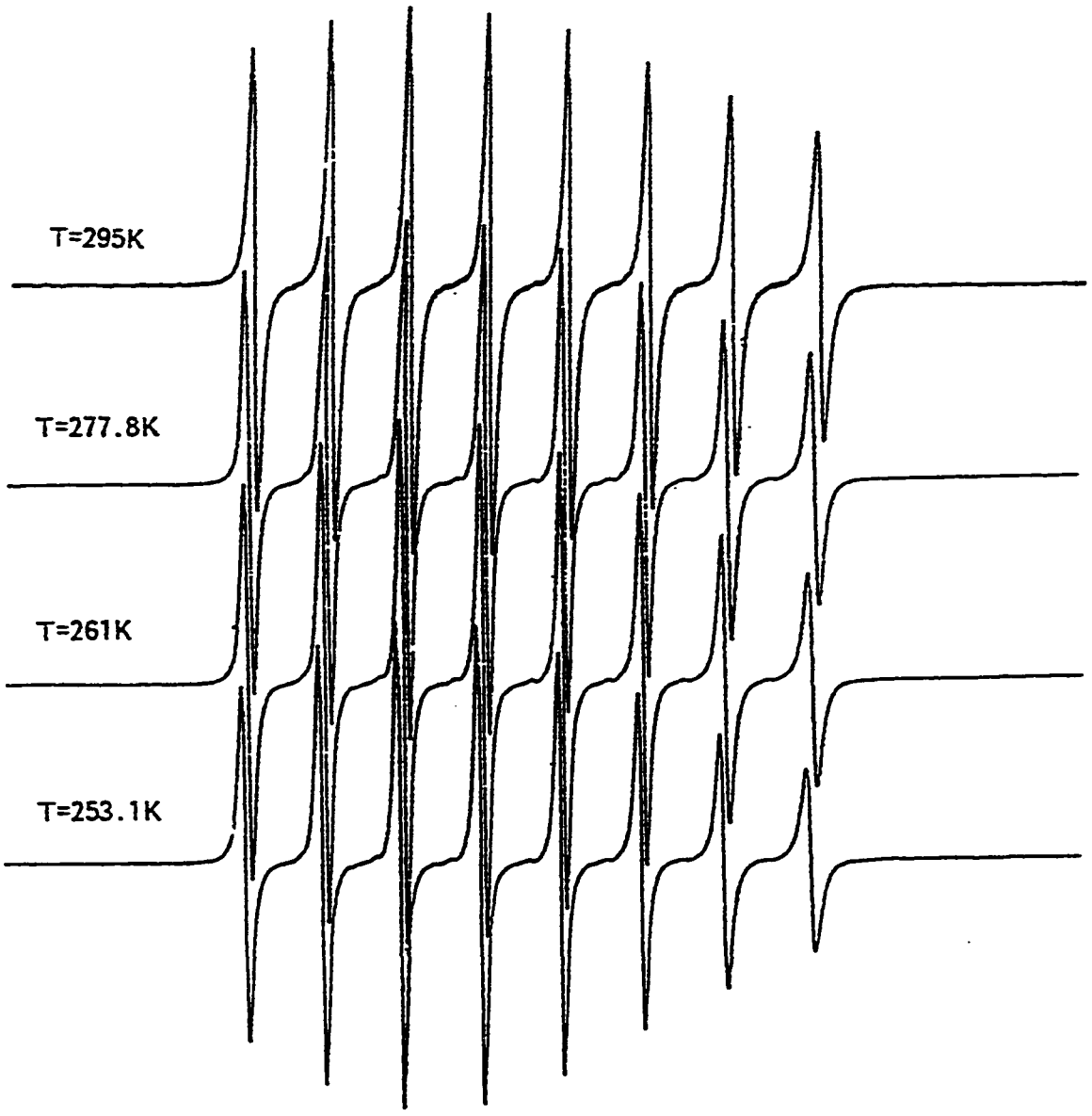

Fig.5.3 : Experimental spectra of Cp_2VCl at Different Temperature

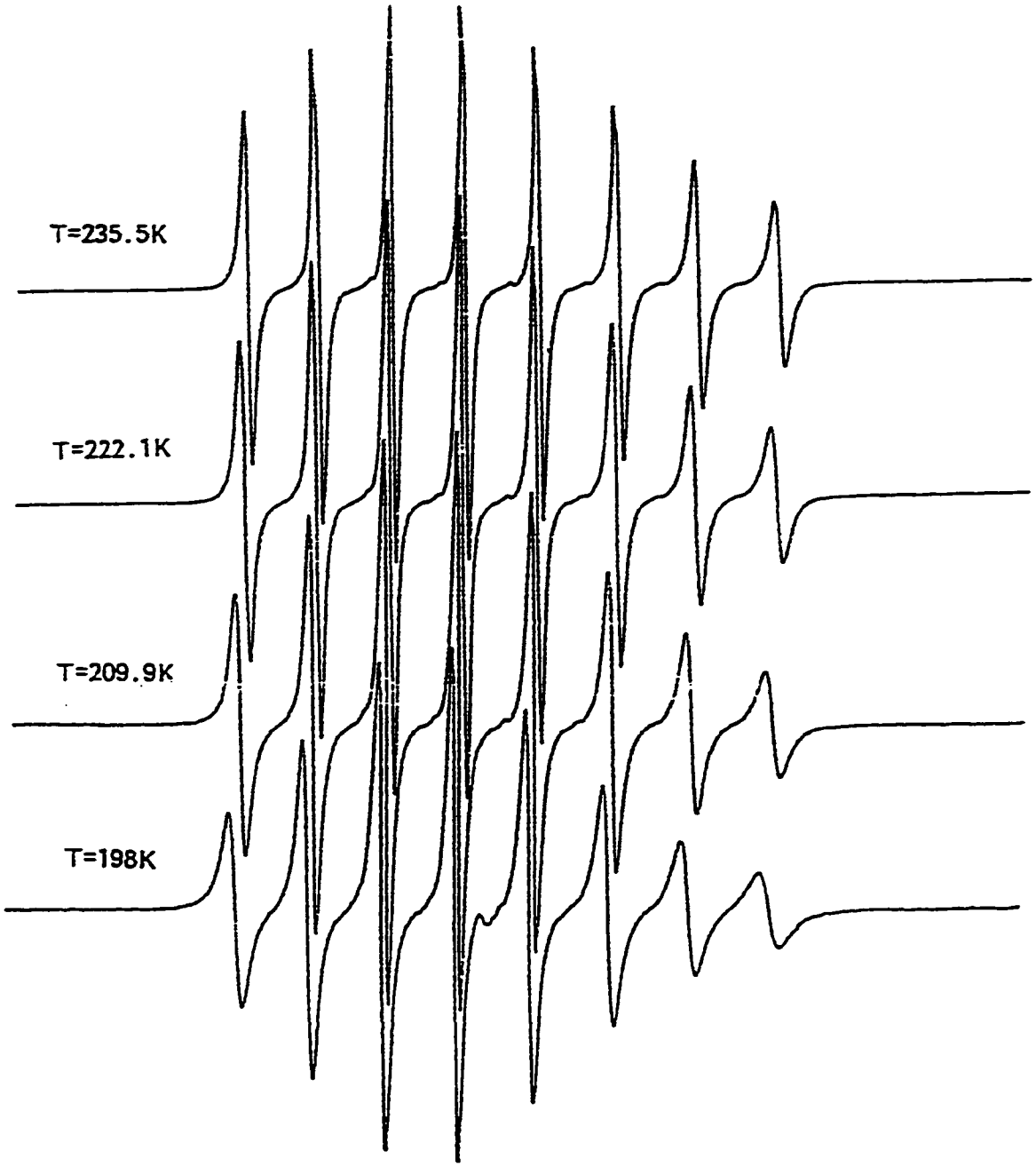

Fig.5.3(cont.) : Experimental Spectra of Cp_2VCl_2 at Different Temperature

Table 5.2 : Experimental Values of Temperature & Lines Widths

Measurement & B & C values

T.oC ΔH(M)	21.7	4.6	-12.2	-20.1	-37.7	-51.1	-63.3	-75.2
ΔH-7/2	6.523	6.475	6.679	6.902	7.598	8.771	10.647	13.757
ΔH-5/2	6.147	6.033	6.081	6.208	6.540	7.216	8.396	10.434
ΔH-3/2	5.982	5.846	5.824	5.888	6.026	6.463	7.223	8.736
ΔH-1/2	6.026	5.900	5.880	5.934	6.042	6.418	7.123	8.497
ΔH+1/2	6.258	6.147	6.223	6.328	6.549	7.066	7.992	9.692
ΔH+3/2	6.664	6.697	6.884	7.094	7.583	8.457	9.922	12.285
ΔH+5/2	7.274	7.448	7.813	8.154	9.088	10.538	12.847	16.433
ΔH+7/2	8.050	8.382	9.056	9.589	11.101	13.361	16.709	21.930
B	.2312	.2864	.3541	.4002	.5202	.6681	.9077	1.207
c	.09568	.1168	.1512	.1759	.2544	.3601	.5103	.7302
C/B	.41384	.4078	.4270	.4395	.4890	.5390	.5622	.6050

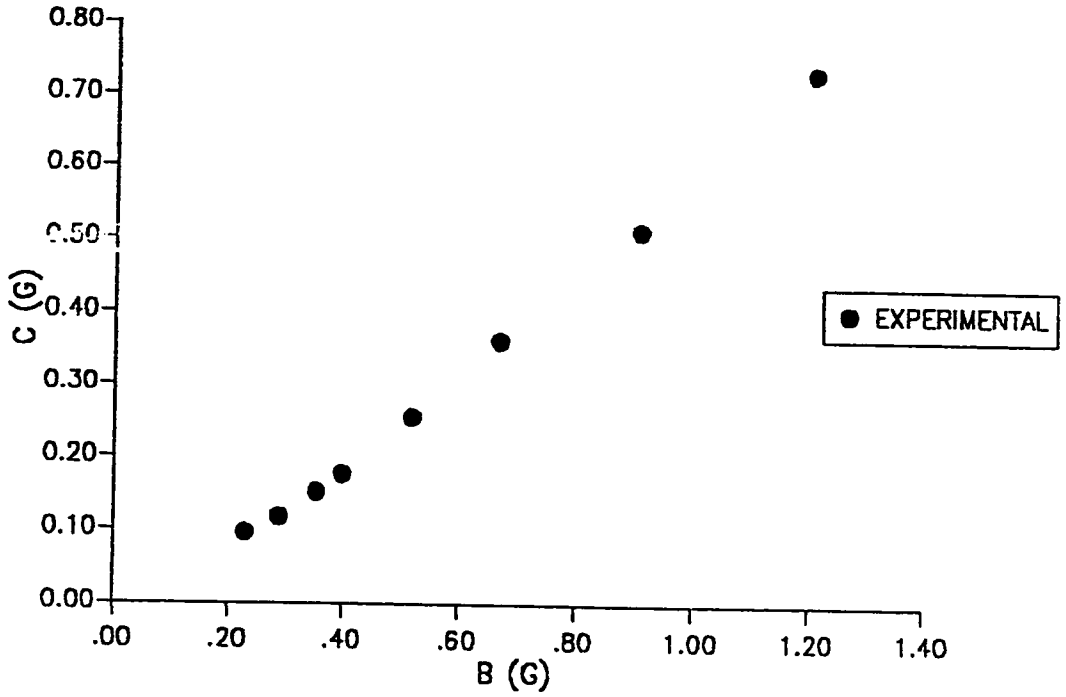

Fig. 5.4 : B Vs C Experimental Values for Cp_2VCl_2 at Different Temperatures.

In order to determine the anisotropy of rotation (N) and the axis of rotation, the theoretical calculations of B and C coefficients which are given by the following equations [59,60] were used. These equations were adopted from the motional-narrowing of Freed et al.[42,43,44].

$$C_o = \frac{8}{3} - [1+(\omega_e\tau_o)^2]^{-1} - \frac{1}{\{3[1+(\omega_o\tau_o)^2]\}} \qquad (5.9)$$

$$C_2 = \frac{8}{3} - [1+(\omega_e\tau_2)^2]^{-1} - \frac{1}{\{3[1+(\omega_o\tau_2)^2]\}} \qquad (5.10)$$

$$C = \frac{2}{\sqrt{3}v}(0.8\pi)^2(D_o\tau_o C_o + 2D_2^2\tau_2 C_2) \qquad (5.11)$$

$$B_o = \frac{16}{3} + \frac{4}{1 + (\omega_o\tau_o)^2} \qquad (5.12)$$

$$B_2 = \frac{16}{3} + \frac{4}{1 + (\omega_2\tau_2)^2} \qquad (5.13)$$

$$B = \frac{-2}{\sqrt{3}v}(0.1\pi\omega_o)(g_1 D_o\tau_o B_o + 2g_2 D_2\tau_2 B_2) \qquad (5.14)$$

where

$$\upsilon = g_o\ (8.7940147x10^6) \quad Sec^{-1}\ G^{-1}$$

$$\upsilon_P = \upsilon \frac{g_o}{g_e}$$

$$g_e = 2.00232$$

$$g_1 = (g_z - g_o)\ (\frac{3}{2})^{\frac{1}{2}}$$

$$g_2 = \frac{(g_x - g_y)}{2}$$

$$\omega_o = 2\ \pi\ \nu$$

$$\omega_\alpha = \frac{A_o\ \upsilon_p}{2}$$

$$D_o = (A_z - A_y)\ (\frac{|\upsilon_p|}{2\pi})\ (\frac{3}{8})^{\frac{1}{2}}$$

$$D_2 = (A_x - A_y)\ (\frac{|\upsilon_p|}{8\ \pi}) \qquad MHz$$

$$\tau_o = \tau_R\ N^{\frac{1}{2}}$$

$$\tau_2 = \frac{3\ \tau_o}{(1+2N)}$$

and the magnetic parameters g's and A's are in table 5.1 .

The theoretical calculations of B and C coefficients are performed by varying τ_R in eqs(5.9, 5.14). The program written for eqs(5.9-5.14) is known as the ABC program (in Basic language). While performing theoretical simulation at the beginning we mainly look at the C/B ratio with the

anisotropic rotational diffusion and reorientation. Basically, the simulation of these curves using eqs(5.9-5.14) involves the fitting of three parameters the C/B ratio, the principal axis of rotation (Z'-axis) and N. Usually the approximate ratio of C/B gives some hint on the Z'-axis . Value of N is then varied to move the upper portion of the curve to approach the experimental points. Appendix 2 shows N, τ_R values and the calculated B and C values for Z' = X, Y, Z, by using the reported magnetic parameters in table 5.1, at frequency of 9.511 GHz . plotting B Vs C for the different values of N for each Z'-axis with the B and C values of the experiment will show for which N value and on which Z'-axis the experimental values is fitted. In Fig. 5.5 we use the magnetic parameter set (a) in table 5.1, it is clear that the experimental points are below the calculated values even by increasing the N values for higher number. Similarly by using the values of set (b) in Fig. 5.6 the experimental points below the calculated one. In Fig. 5.7, by using set (c) values, the experimental points come above the calculated values. Fig. 5.8 by using set (d), shows that at Z'=X and Z the experimental points come above the calculated line, but at Z'=Y and for N=2.7 the experimental points are on the calculated line.

This suggest that Cp_2VCl_2 has a preferential rotation axis Z'=Y at N=2.7 over the other two axes. In Fig. 5.9 we compare all sets (a,b,c,d) at Z'=Y and N=2.7 to show clear fitting of the experimental values with the calculated one. Also in Fig. 5.10 we show the effect of changing the frequency on the fitting which is small effect.

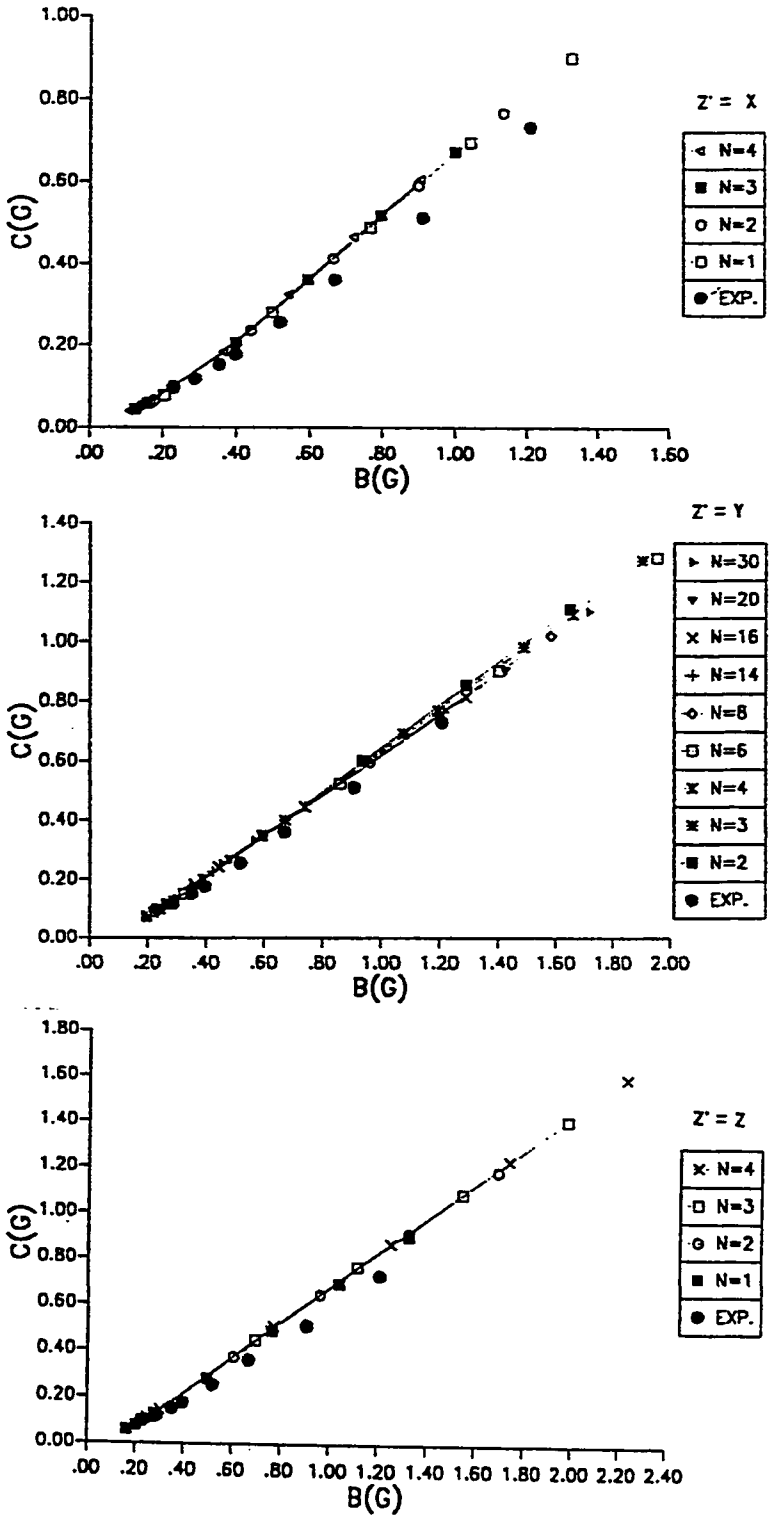

Fig. 5.5 : Experimental fit using the magnetic parameter set(a) for Z'=X,Y,Z

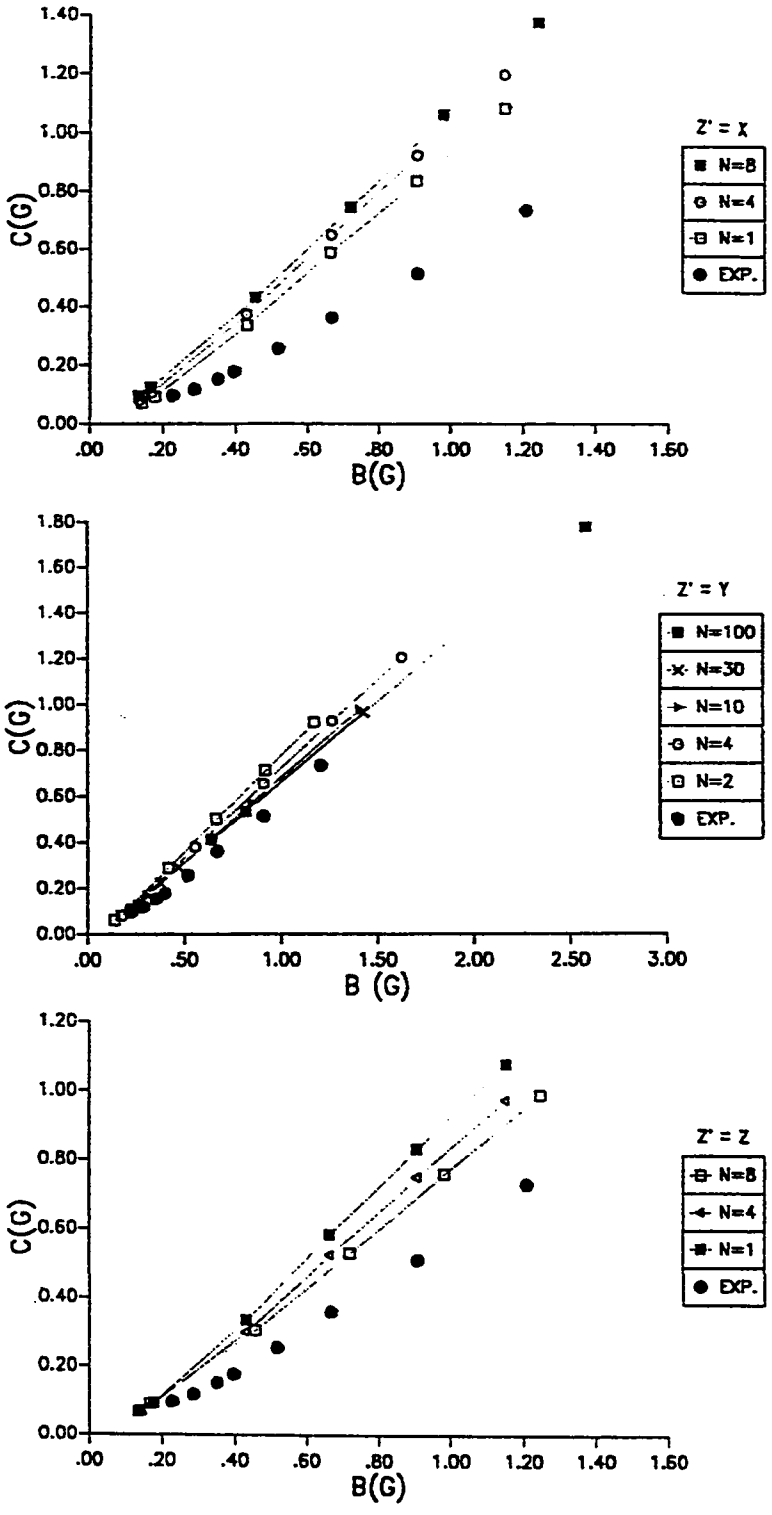

Fig. 5.6 : Experimental fit using the magnetic parameter set(b) for Z'=X,Y,Z

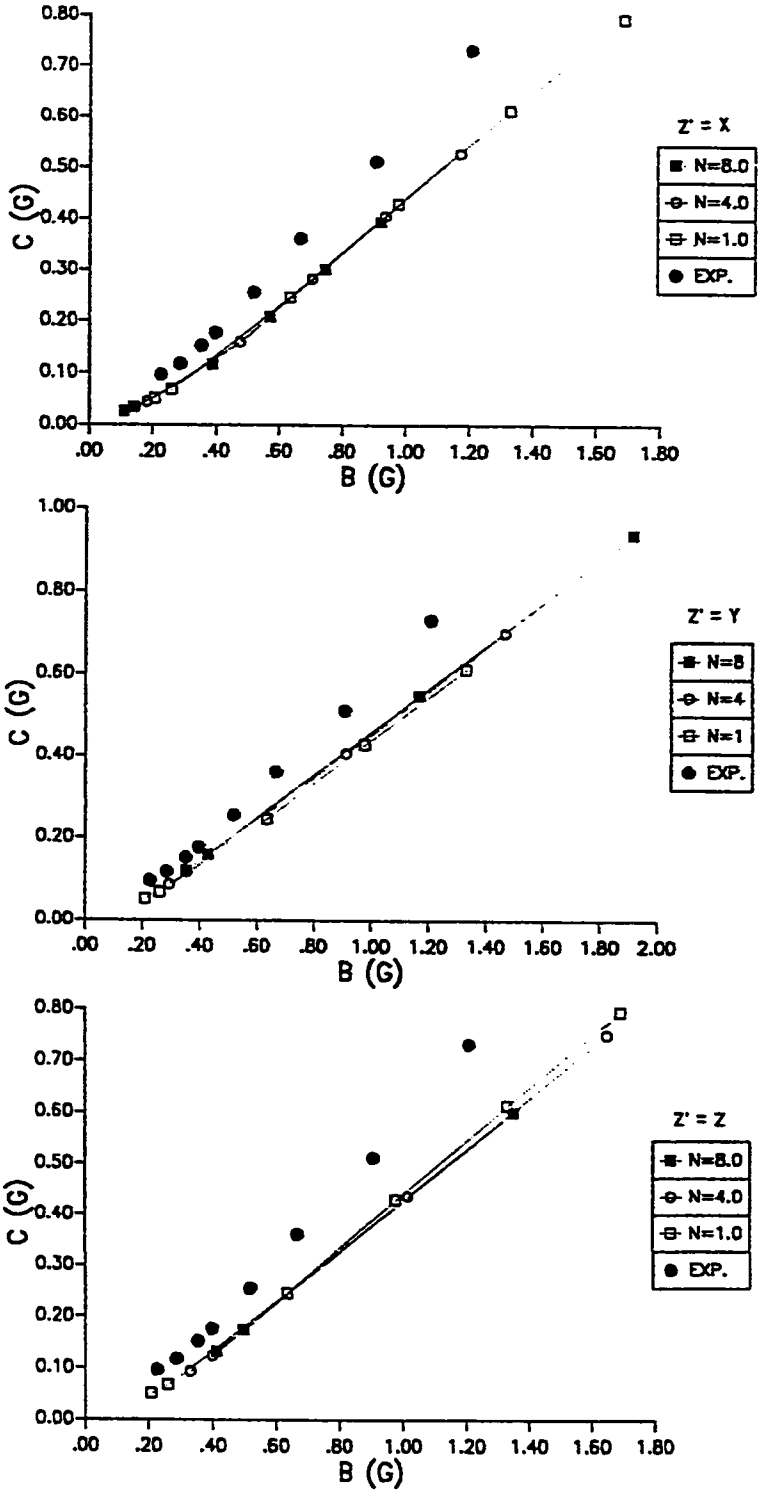

Fig. 5.7 : Experimental fit using the magnetic parameter set(c) for Z'=X,Y,Z

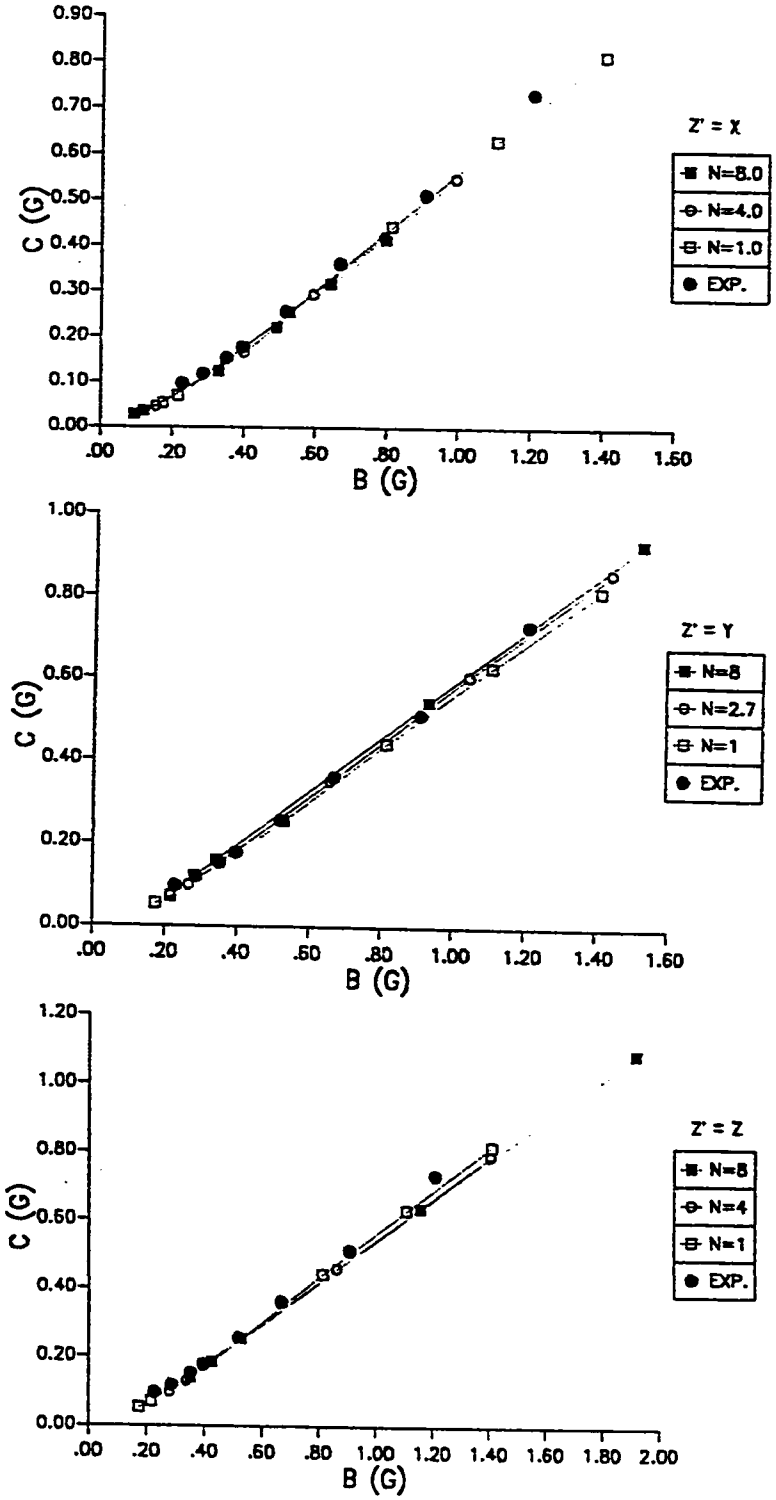

Fig. 5.8 : Experimental fit using the magnetic parameter set(d) for Z'=X,Y,Z the best fit at Z'=Y and N=2.7

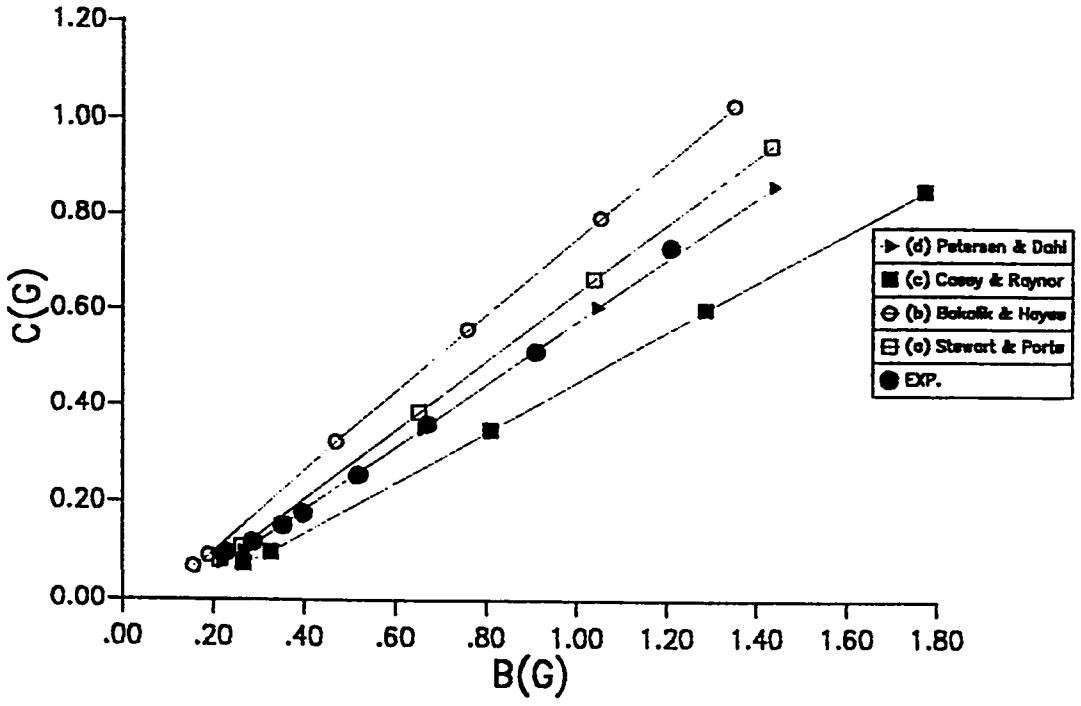

Fig. 5.9 : Experimental fit using the magnetic parameter sets(a,b,c,d) for Z'=Y and N=2.7

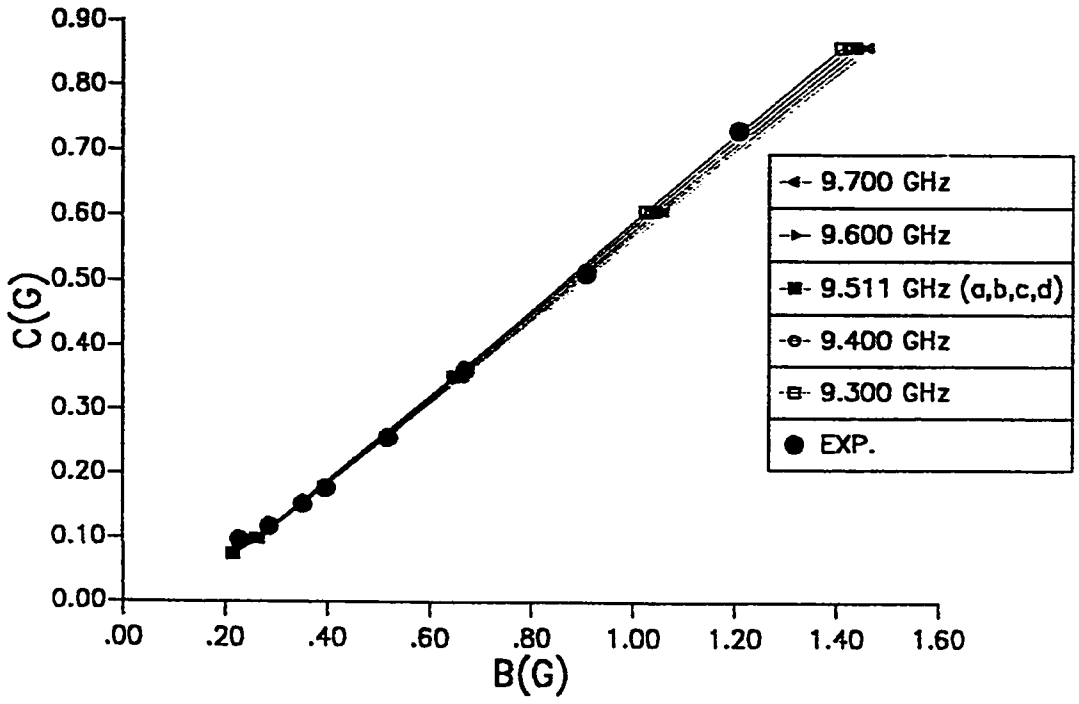

Fig. 5.10 : Experimental fit using the magnetic parameter set(d) for Z'=Y and N=2.7 at different frequency.

Form the best fit plot in (Fig.5.8) one can generate an other plot between the C theoretical values Vs. τ_R (table 5.3), then we can extrapolate the experimental values C to fined τ_R experimental values from the straight line equation of C Vs. τ_R of the theoretical values, as in Fig.5.11 . By knowing the experimental τ_R at different temperature and the viscosity at different temperature we can use eq.(1.2) to find the relation (slope), if we plot the correlation time τ_R Vs. $\eta/T(K)$ for this experimental values as in Fig.5.12 . The viscosity values for toluene is corrected for different temperature using [61] the following equation,

$$\eta = \frac{a}{(b + t)^n} \qquad (5.15)$$

where, a = 18.954 , b = 112.99 , n = 1.6522, t the temperature in(^{0}C), the calculated value of η is in poise. Table 5.4 show the results. The slope we get is equal to

$$\textit{The Slope} = \left(\frac{4}{3}\,\pi\, r_o^3\right)\left(\frac{\kappa}{k_B}\right)$$

where the first bracket term is the volume of the molecule and the value of r_0 will be determine in the next experimental result from the translational diffusion constant, from which we can recalculate κ (the anisotropic interaction parameter) instead of estimating its volume by computer program or other method. The value of the slope is = 2.6823×10^{-7} sec KP^{-1}, by using the first seven point (corr.=0.9993) instead of (corr. =0.9951) for all eight points.

Table 5.3 : Theoretical values of B & C & τ_l for Z'=Y and N=2.7

τ_l(sec x10^{-11})	B (G)	C (G)
0.688	0.2168	0.07376
0.888	0.2658	0.09757
2.880	0.6578	0.3502
4.880	1.042	0.6053
6.880	1.435	0.8599
8.880	1.833	1.115

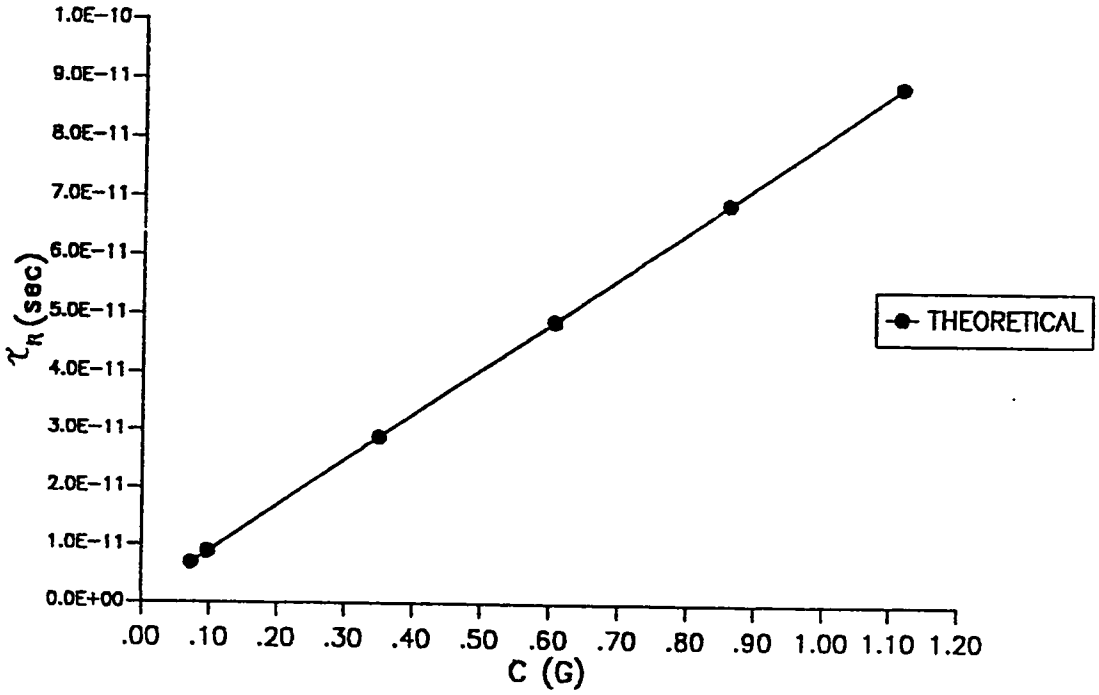

Fig. 5.11 : C Vs. τ_R theoretical values

Table 5.4 : η , η/T and τ_R Values for Cp_2VCl_2 Experiment

t (^{0}C)	η (P x10^{-2})	η/T(PK^{-1}x10^{-4})	τ_R(Sec.x10^{-11})
21.7	0.57493	0.19500	0.87059
4.6	0.71951	0.25906	1.03664
-12.2	0.92823	0.35573	1.30709
-20.1	1.0622	0.41979	1.50128
-37.7	1.5030	0.63837	2.11845
-51.1	2.0777	0.93574	2.94947
-63.3	2.9862	1.4231	4.13035
-75.2	4.6942	2.3715	5.85921

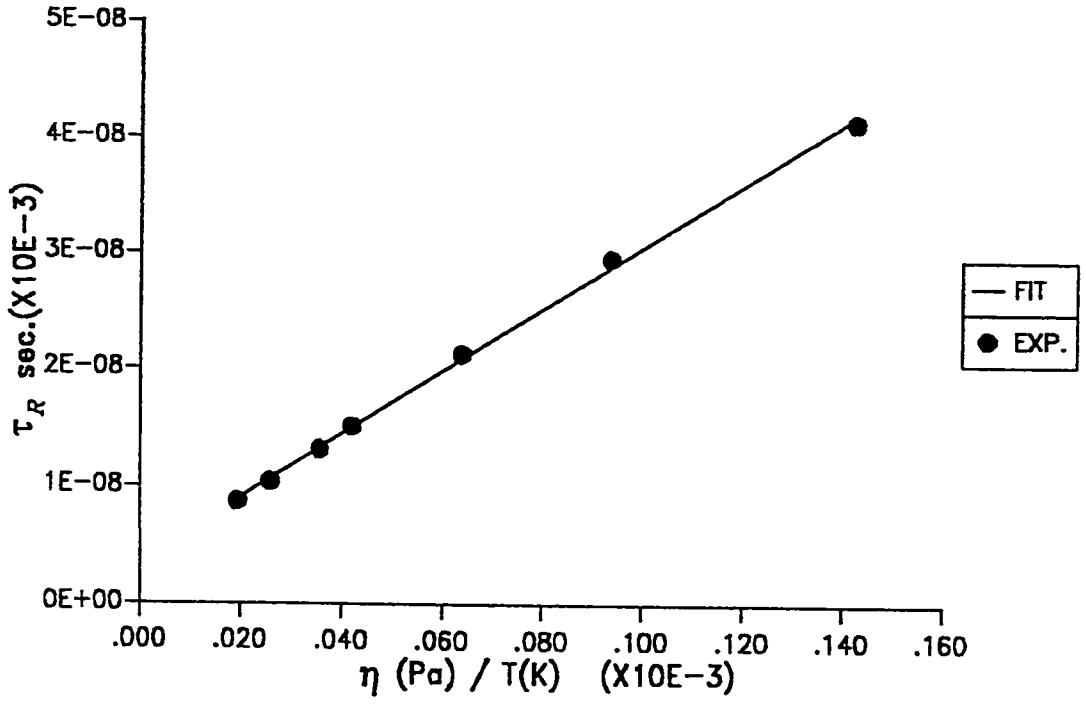

Fig. 5.12 : η/T Vs. τ_R for Cp_2VCl_2 in toluene.

5.3 : DETERMINATION OF THE TRANSLATIONAL DIFFUSION CONSTANT

5.3.1 Cp_2VCl_2

The capillary diffusion experiment which described in chapter three is done for Cp_2VCl_2 as mention. The experiment takes abut 22 days , from which 57 spectra are collected. The time is recorded for each run and each spectra is analysis to find the intensities of the eight lines (if the intensities dropped much at short time this give a result that high concentration difference between the solution in the capillary and the solvent above it, so the experiment will continue until a steady state start, then readjust the ESR spectrum parameter to get maximum intensities again Fig.5.13 show this effect). The data are introduce to the program " DIFF.FORTRAN " and the best least square fit is result form which the time and intensity for this spectra is substituted in eq.(1.13) to get the diffusion constant, and the value is recalculated by the fitting coefficients , also the ratio R ($R = \ell_s / \ell_t$) is recalculated to check the experimental data. The line widths is calculated and adjusted by the following ,

$$\Delta\omega_i = \Delta\omega_o \ (I_o/I_i)^{\frac{1}{2}} \qquad (5.16)$$

$\Delta\omega_0$ and I_0 is the line width and intensity of a reference line and in Cp_2VCl_2 it the line of $M = -1/2$, $\Delta\omega_i$ and I_i is the line width and intensity for a particular line, the average line widths is calculated and given by the program. The relative total intensity for each spectra and the time is in table 5.5 . In (Fig.5.14) some full spectra are shown. From the diffusion constant the program generate the fitting curve points (time Vs. intensity) which is plotted with the experimental values in (Fig. 5.15). In Appendix 1 the computer program, the input data and the output calculation is given for Cp_2VCl_2 . The diffusion constant calculated by the DIFF. computer program for Cp_2VCl_2 is = 0.520×10^{-5} cm^2/s
The value of R(= ℓ_s / ℓ_t) simulated is with in experimental error R(exp)=0.57143, R(cal.)=0.5700 .

5.3.2 VO[5-MeO-Sal SB](Phen)

For this compound the experiment goes for abut 25 days and 62 spectra were taken , some of the spectra are shown in Fig.5.16. The full data are in appendix.1 as computer output also the calculation of total intensity and time is given . A plot of time vs. intensity is in Fig.5.17 with a simulation of the result, the value of diffusion constant obtained for VO[5-MeO-Sal SB](Phen) is = 0.655×10^{-5} cm^2/sec .
The value of R(= ℓ_s / ℓ_t) simulated is with in experimental error R(exp)=0.57143, R(cal.)=0.6800 .

Table 5.5 : Time and Intensity of Cp_2VCl_2 diffusion

p.#	Time(Sec)	Intensity	p.#	Time(Sec)	Intensity
* 1	$0.240x10^3$	1.000	30	$0.860x10^6$	0.451
2	$0.480x10^5$	0.966	31	$0.901x10^6$	0.439
3	$0.744x10^5$	0.961	32	$0.927x10^6$	0.416
4	$0.876x10^5$	0.951	33	$0.940x10^6$	0.407
5	$0.138x10^6$	0.912	*34	$0.986x10^6$	0.394
6	$0.153x10^6$	0.909	35	$0.101x10^7$	0.384
* 7	$0.173x10^6$	0.893	36	$0.104x10^7$	0.370
8	$0.212x10^6$	0.862	37	$0.107x10^7$	0.359
9	$0.241x10^6$	0.826	38	$0.107x10^7$	0.337
10	$0.259x10^6$	0.831	39	$0.112x10^7$	0.335
11	$0.297x10^6$	0.806	*40	$0.117x10^7$	0.312
12	$0.318x10^6$	0.791	41	$0.119x10^7$	0.298
13	$0.346x10^6$	0.756	42	$0.121x10^7$	0.307
*14	$0.381x10^6$	0.751	43	$0.125x10^7$	0.291
15	$0.409x10^6$	0.718	44	$0.127x10^7$	0.284
16	$0.431x10^6$	0.706	45	$0.130x10^7$	0.273
17	$0.469x10^6$	0.687	46	$0.133x10^7$	0.266
18	$0.498x10^6$	0.657	47	$0.136x10^7$	0.256
19	$0.512x10^6$	0.651	*48	$0.138x10^7$	0.244
20	$0.555x10^6$	0.634	49	$0.142x10^7$	0.238
*21	$0.579x10^6$	0.615	50	$0.144x10^7$	0.222
22	$0.604x10^6$	0.590	51	$0.147x10^7$	0.226
23	$0.667x10^6$	0.556	52	$0.151x10^7$	0.226
24	$0.690x10^6$	0.543	53	$0.155x10^7$	0.208
25	$0.727x10^6$	0.522	54	$0.159x10^7$	0.192
26	$0.758x10^6$	0.510	55	$0.169x10^7$	0.172
*27	$0.778x10^6$	0.497	*56	$0.180x10^7$	0.151
28	$0.815x10^6$	0.472	57	$0.188x10^7$	0.145
29	$0.843x10^6$	0.466			

*The spectra shown in Fig. 5.14 .

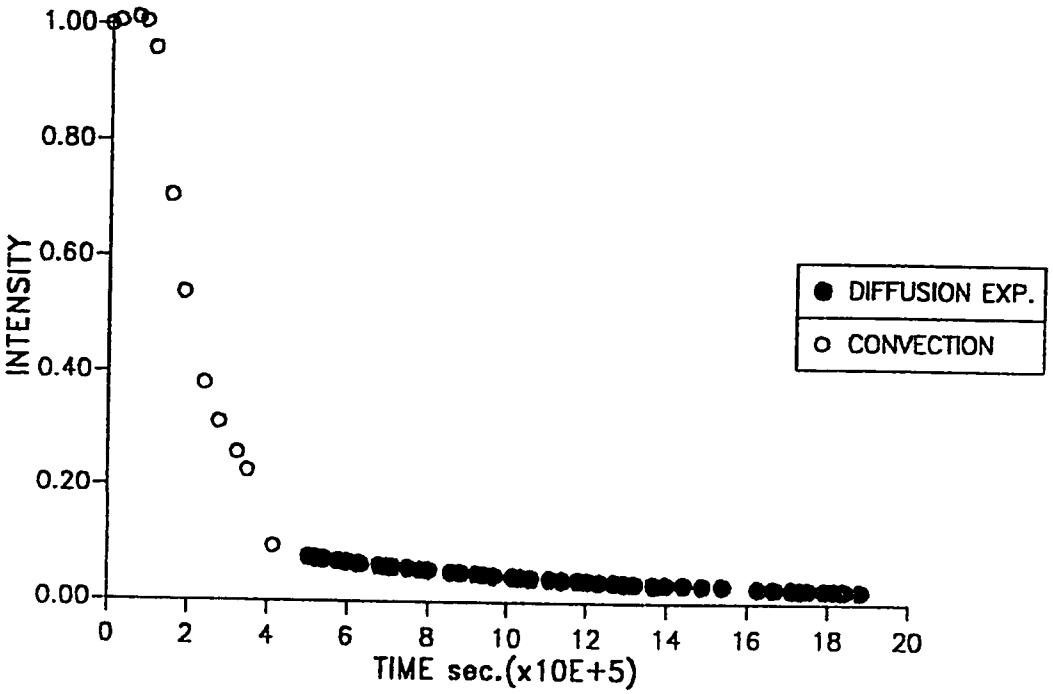

Fig. 5.13 : The effect of high concentration on diffusion.

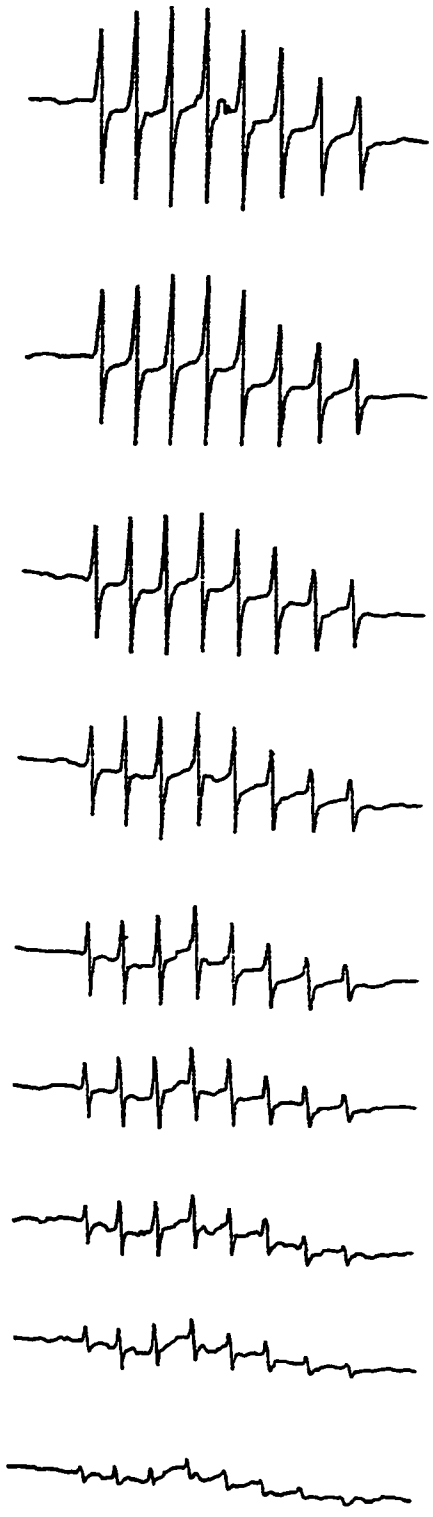

Fig. 5.14 : First derivative ESR spectra of Cp_2VCl_2 at different time, the time and total intensity is marked (*) in table 5.5 .

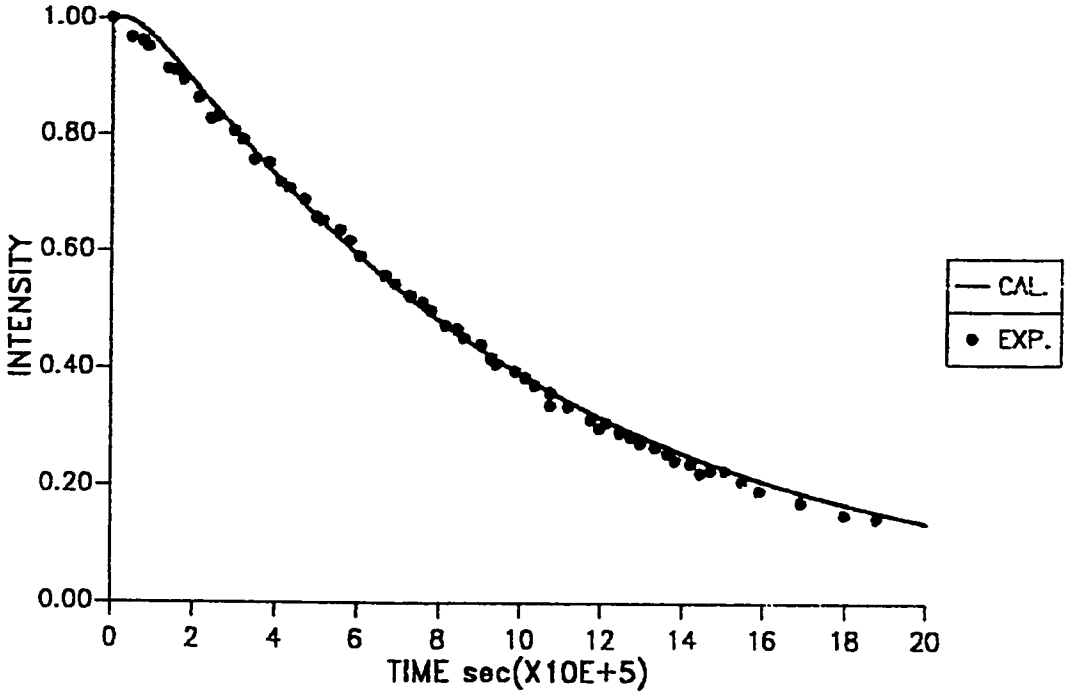

Fig. 5.15 : Total ESR intensities as a function of time for Cp_2VCl_2

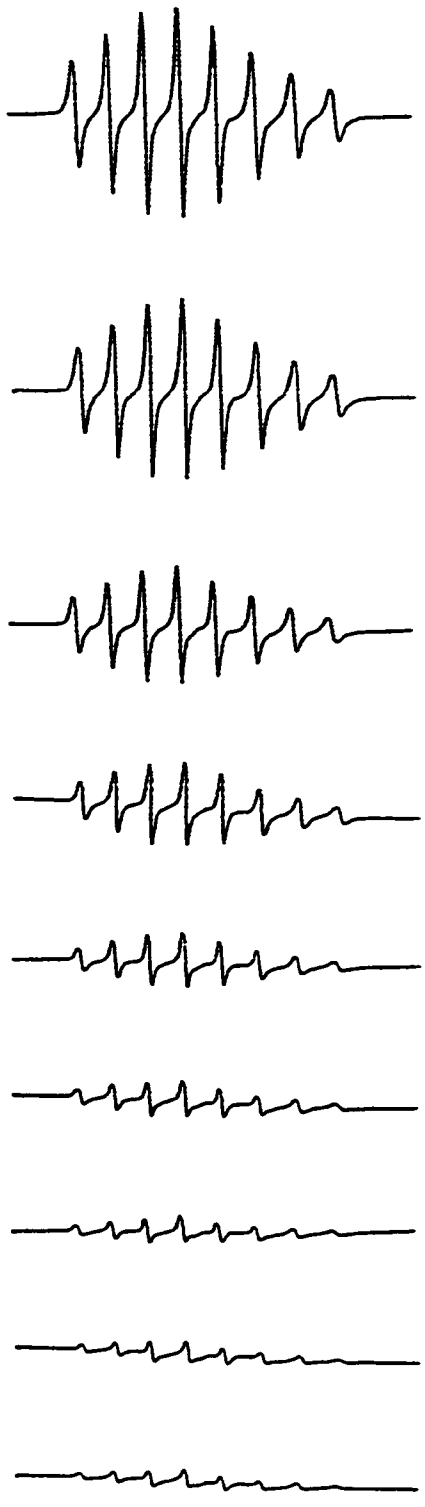

Fig. 5.16 : First derivative ESR spectra of VO[5-MeO-Sal SB](Phen) at different time.

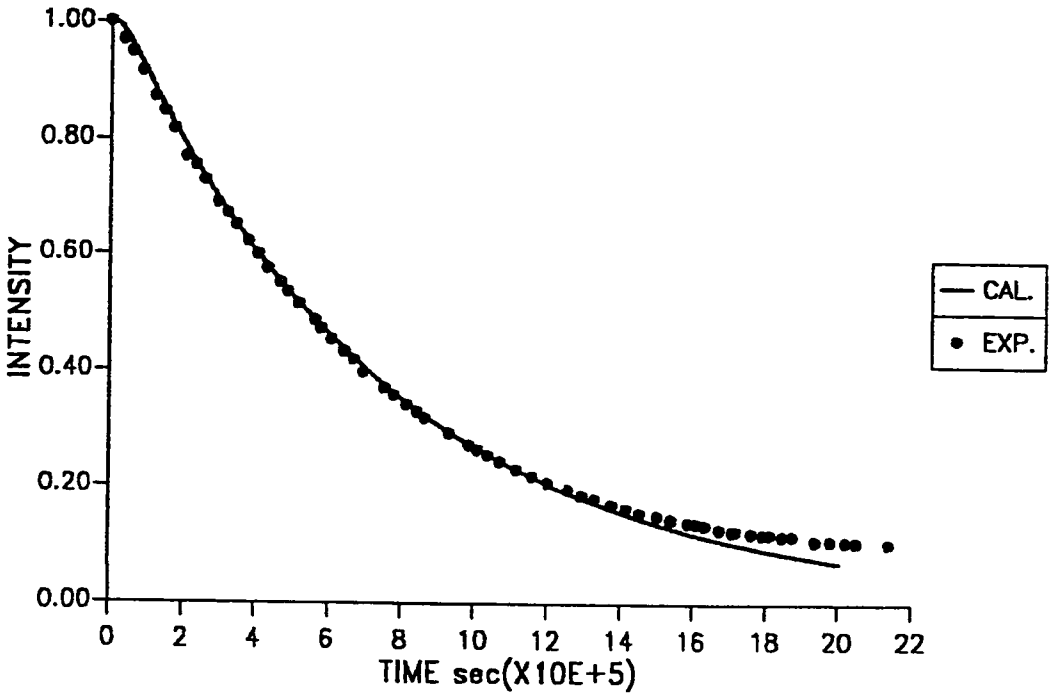

Fig. 5.17 : Total ESR intensities as a function of time for VO[5-MeO-Sal SB](Phen)

5.3.3 The Hydrodynamic radius

To calculate the hydrodynamic radius of these compound one can use Stokes-Einstein equation(1.1), by substituting the values obtained for the diffusion constant and the other parameter the unit for each are, D in cm^2/sec, k in JK^{-1}, T room temperature in K, η in Pa.sec, by multiplying with a factor of (10^{14}) the hydrodynamic radius results in (Å).

This hydrodynamic radius actually is the diameter of the molecules since it is rotating as sphere, so the radius of it will be half of the value obtained from the equation , to get the volume of the molecule by using the formula of the sphere volume ($4 \pi {}^3r_0 / 3$). The value results are in the next table,

Compound	Hyd.radius(Å)	Radius(Å)	Volume($Å^3$)
Compound I	7.820	3.910	250.0
Compound II	8.073	4.036	275.0

Compound I : Cp_2VCl_2

Compound II : VO[5-MeO-Sal SB](Phen)

5.3.4 Simulating The Molecular Volume from Disk Top Molecular Model [DTMM]

A computer program available for drawing the molecular structure and minimizing the energy of the molecules by iteration to minimize the torsional angle , Van der waals forces, and other effect. Then it produce a structure that can be compare with the real molecule, looking at it from different angel and position and rotation on different axis carefully we can measure at least three lengths to determine the volume of this molecule , the structures are shown in Fig.5.18 for the two compound under study and a module compound vanadyl bisacetylacetonate or [VOAA], Fig.5.19 is the crystal structure of VOAA. The lengths obtained for the compounds are

Compound	r_1(Å)	r_2(Å)	r_3(Å)
Compound I	5.78	7.73	4.27
Compound II	8.6	13.5	6.4

Compound I : Cp_2VCl_2 , Compound II : VO[5-MeO Sal SB](Phen)

where r_1, r_2 , r_3 are the length between two atoms in the same plane. Looking at the two tables above we can correlate between the hydrodynamic radius of the first compound (I) and the value of r_2 , similarly for compound (II) the hydrodynamic radius is comparable with r_1 , this give some indication that these compounds are rotating along these axis.

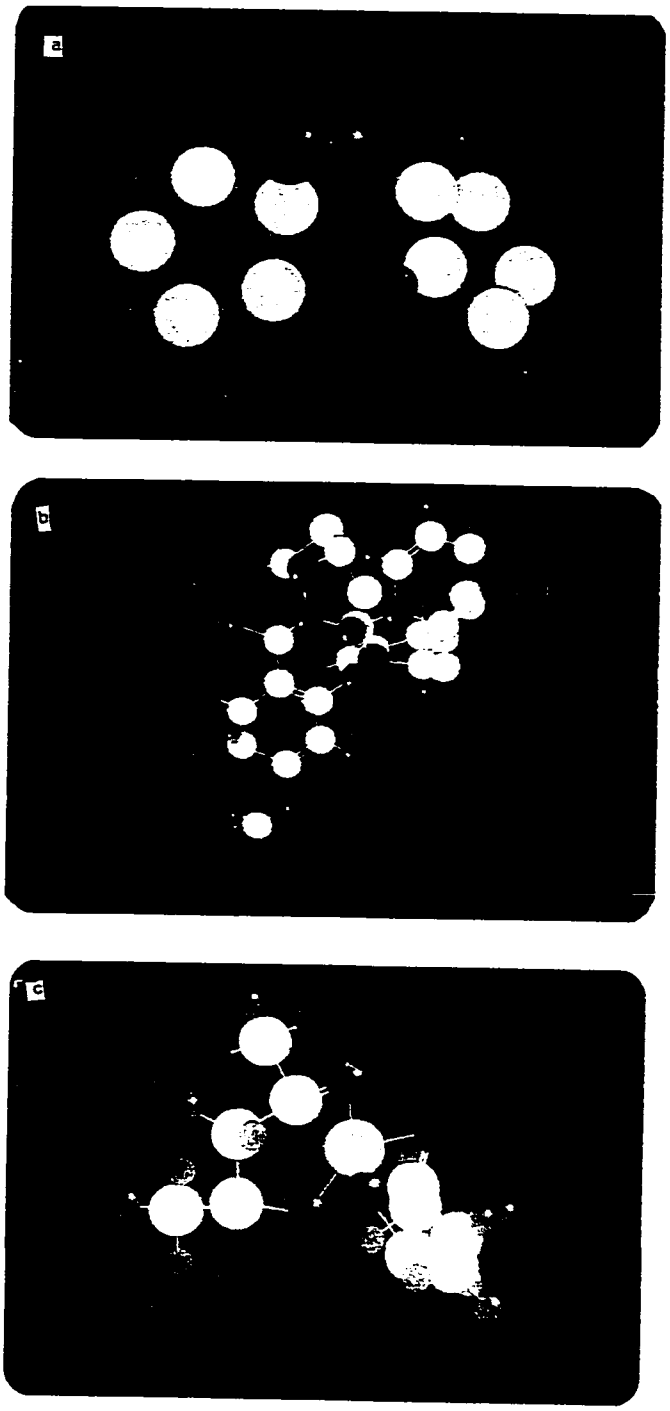

Fig. 5.18 : Structures by DTMM program,(a) Cp_2VCl_2, (b) VO[5-MeO Sal SB](Phen) , (c) VOAA

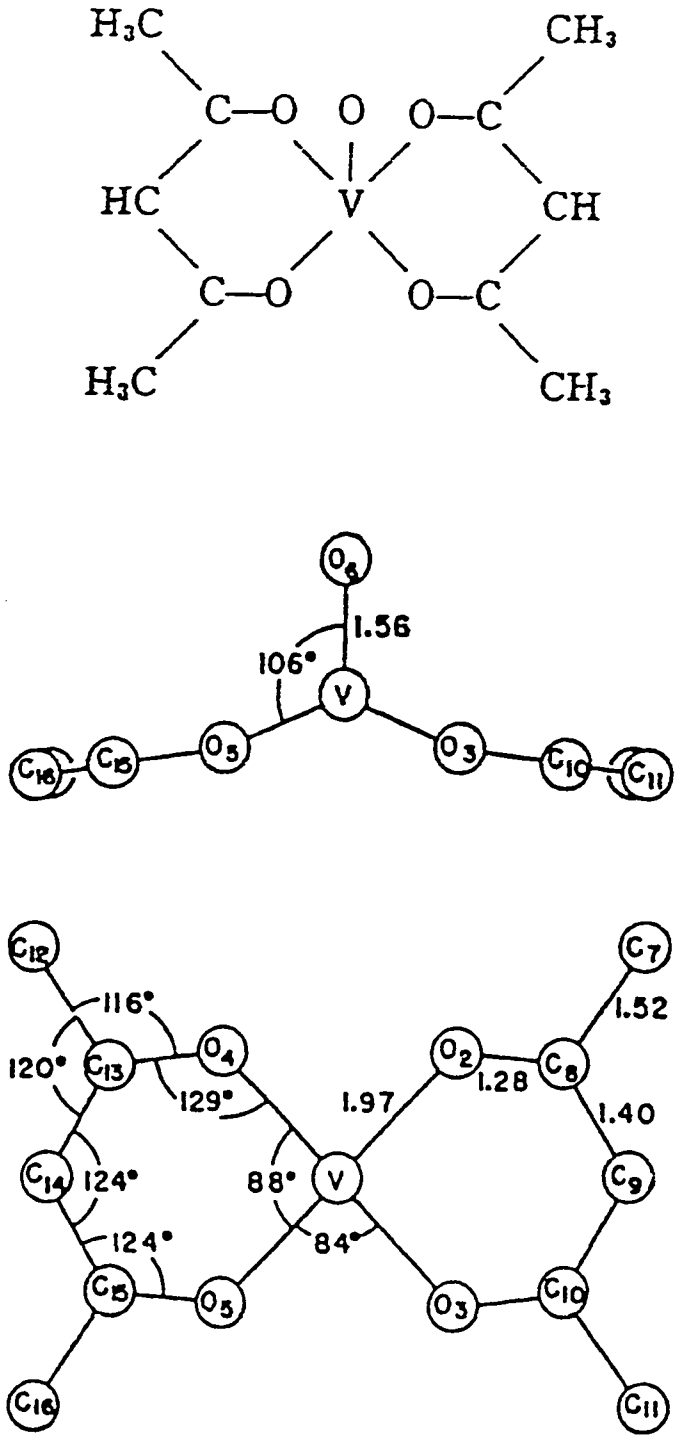

Fig. 5.19 : Crystal Structure of VOAA

5.4 ANISOTROPIC INTERACTION PARAMETER (κ)

In previous discussion in section 5.2 for Cp_2VCl_2 we end with the slope value results from plotting (η/T) Vs. τ_R which are related by eq.(1.2), the slope is equal to

$$\textit{The Slope} = \left(\frac{4}{3}\,\pi\, r_o^3\right)\left(\frac{\kappa}{k_B}\right)$$

to get κ we substitute by the volume in ($\AA^3$), the slope in ($sec.Pa.K^{-1}$), and k_B in (JK^{-1}), then a factor of (10^{31}) is multiplied to get κ as dimensionless unit,

κ = (slope) (k_B) (10^{31}) / volume

= (2.6823×10^{-7})(1.381×10^{-23})(10^{31})/(250.0)

κ = 0.150

5.5 STICKINESS FACTOR (S)

We can analyzed the data for Cp_2VCl_2 which we get from DTMM program in term of hydrodynamic free space model for molecular relaxation in liquids[63], a theory based on the existence of free space in the hydrodynamic continuum in which the molecule can rotate. We assign the major axis $r_{\parallel} = 7.73$ $r_{\perp} = 5.78$, the symmetry parameter $\alpha^{\perp}$ is defined as $(r_{\perp}/r_{\parallel})$. Under stick boundary conditions, where the fluid at the surface of the rotating body sticks to it [68], the dimensionless rotational friction coefficient can be calculated from Perrin's formula [64],

$$f^{\perp}_{stick} = \frac{(2/3)\,[1-(\alpha^{\perp})^4]}{\dfrac{[2-(\alpha^{\perp})^2]\,(\alpha^{\perp})^2}{[1-(\alpha^{\perp})^2]^{\frac{1}{2}}} \ln\left|\dfrac{1+[1-(\alpha^{\perp})^2]^{\frac{1}{2}}}{\alpha^{\perp}}\right| - (\alpha^{\perp})^2} \qquad (5.17)$$

$\alpha^{\perp} = 0.747$. This gives $f^{\perp}_{stick} = 1.11$. The corresponding value of the dimensionless rotational friction coefficient under slip boundary condition, $f^{\perp}_{slip}$, is calculated from

$$f^{\perp}_{slip} = f^{\perp}_{stick}\,[1-(f^{\perp}_{stick})^{\frac{-2}{3}}] \qquad (5.18)$$

the value of $f^{\perp}_{slip} = 0.0761$

from the relation,

$$f^{\perp}_{slip} = f^{\perp}_{stick}\;\; C^{hyd}_{slip} \qquad (5.19)$$

we can calculate

$$C^{hyd}_{slip} = 0.0761/1.111 = 0.0685$$

The stickiness factor, S is independent of molecular geometry and is zero in the slip limit and 1 in the stick limit. For truly hydrodynamic situation $0 \leq S \leq 1$, from eq.(1.3) we can calculate

$$S = (0.150-0.0685)/(1-0.0685) = 0.0875 \quad .$$

5.6 STOKES-EINSTEIN MODEL

The anisotropy for rotation (N) , defined as $N = R_{\parallel}/R_{\perp}$ is related to the geometric structure factor by means of the Stokes-Einstein equation[11,59,60],

$$R_i = \frac{k_B T}{(8\pi\eta r_{\parallel}^3 \sigma_i)}, \qquad i = \parallel \text{ or } \perp \tag{5.20}$$

where,

$$N = \frac{R_{\parallel}}{R_{\perp}} = \frac{\sigma_{\perp}}{\sigma_{\parallel}} \tag{5.21}$$

$$\sigma_{\parallel} = \frac{2}{3} \lambda^2 (1+\lambda^2) [(1+\lambda^2) \lambda^{-1} \tan^{-1} \lambda - 1]^{-1} \tag{5.22}$$

$$\sigma_{\perp} = \frac{2}{3} \lambda^2 (2+\lambda^2) [1-(1-\lambda^2) \lambda^{-1} \tan^{-1} \lambda]^{-1} \tag{5.23}$$

and λ is a dimensionless structure factor,

$$\lambda = \frac{(r_{\parallel}^2 - r_{\perp}^2)^{\frac{1}{2}}}{r_{\perp}} \qquad (5.24)$$

From the DTMM program data,

$r_{\parallel} = 7.73$

$r_{\perp} = 4.28,$

$\lambda = 1.504$

$\sigma_{\parallel} = 0.0405$

$\sigma_{\perp} = 0.133$

$N = 3.28$

which is within experimental error, with our observation that is $N = 2.7 \pm 0.5$.

5.7 THE ALLOWED - VALUES EQUATION (AVE)

An alternative approach to the determination of N is through the use of the allowed-values equation,

$$A\,\rho_x = B\,\rho_y + C \qquad (5.25)$$

derived by Kowert [45,60] from line width coefficients B and c when nonsecular terms are unimportant, which shows that only one value of $\rho_1 = R_1/R_2$ is consistent with a C/B ratio obtained from experiment for a given $\rho_1 = R_1/R_2$. If we let $C = \gamma$ and $B = \beta$, then

$$A = (\Delta a - 3\delta a)[(\gamma/\beta)(\Delta g^- - 3\delta g^-) - (5/16)(\Delta a - 3\delta a)] \qquad (a)$$

$$B = (\Delta a + 3\delta a)[(5/16)(\Delta a + 3\delta a) - (\gamma/\beta)(\Delta g^- + 3\delta g^-)] \qquad (b)$$

$$C = 4\Delta a[(5/16)\Delta a - (\gamma/\beta)\Delta g^-] \qquad (c)$$

with

$$\Delta a = a_1 - (\tfrac{1}{2})(a_1 + a_1) \qquad (d)$$

$$\delta a = (\tfrac{1}{2})(a_1 - a_1) \qquad (e)$$

$$\Delta g^- = [g_1 - (\tfrac{1}{2})(g_1 + g_1)](\beta H_0/\hbar) \qquad (f)$$

$$\delta g^- = (\tfrac{1}{2})(g_1 - g_1)(\beta H_0/\hbar) \qquad (g)$$

and

$$\rho_1 = R_1/R_2 \qquad (h)$$

$$\rho_1 = R_1/R_2 \qquad (i)$$

The values of the various expressions in Eqs. (a-g) using the magnetic parameters g's and a's of set (d) in table 5.1 are listed as follows (in Hz),

$\Delta a = 1.426 \times 10^{9}$

$\delta a = 3.850 \times 10^{8}$

$\Delta g^{-} = 7.956 \times 10^{8}$

$\delta g^{-} = 1.609 \times 10^{8}$

$A = 2.834 \times 10^{16}$

$B = 8.572 \times 10^{16}$

$C = -2.040 \times 10^{17}$

Using C/B value of 0.605 determined experimentally in table 5.2, the allowed-values equation is

$$2.834 \times 10^{16} \ \rho_{Y} = 8.572 \times 10^{16} \ \rho_{I} - 2.040 \times 10^{17} \qquad (j)$$

Dividing the equation by 2.834×10^{16} gives

$$\rho_{Y} = 3.02 \ \rho_{I} - 7.20 \qquad (k)$$

Equation (k) is not consistent with isotropic reorientation and only consistent with axial symmetry if $\rho_{Y} = 1$, $\rho_{I} = 2.71$. The allowed-values equation is very sensitive to variation in the γ/β value. The N obtained by using the allowed-values equation is $N = 2.71 \pm 0.5$. This result is consistent with the value determined from motional - narrowing results and the Stokes-Einstein model.

5.8 CONCLUSION

The translational diffusion constant of Cp_2VCl_2 in chloroform has been measured by the capillary diffusion method at room temperature. The translational diffusion processes were monitored by electron spin resonance spectral intensities as a function of time. A computer program based on Fick's second law of diffusion for the capillary diffusion cell was written to get a single value of the diffusion constant. From the best least squares fit of the total intensities as a function of time a single value of the translational diffusion coefficient of 0.520×10^{-5} cm^2/s was found for Cp_2VCl_2 in chloroform measured at room temperature (25 ± 1 °C). Using Stokes-Einstein equation for translational diffusion, the hydrodynamic volume of Cp_2VCl_2 in chloroform was found to be 250 $Å^3$. And for VO[5-MeO-Sal SB](Phen) the diffusion constant is 0.655×10^{-5} cm^2/s , the volume is 275 $Å^3$.

From an analysis of the temperature dependent ESR line width of Cp_2VCl_2 in toluene in the motional narrowing region it was found that (1) of the four sets of the magnetic parameters for Cp_2VCl_2 available in the literature, only one set of magnetic parameters by Petersen and Dahl could be used to explain the line width data, and (2) Cp_2VCl_2 in toluene was undergoing anisotropic reorientation with N = 2.7 ± 0.5 at an axis z' = Y, where N is the ratio of $R_\parallel/R_\perp$ and $R_\parallel$ is the rotational diffusion constant along the molecular Z axis and

R_I is the rotational diffusion constant perpendicular to the molecular Z axis. This conclusion is also supported by the analysis of anisotropic and nonsecular contributions to the ESR line widths using the allowed-values equation. The AVE analysis for Cp_2VCl_2 in toluene gives $\rho_X = 3.02\ \rho_Y - 7.20$ which is not consistent with isotropic reorientation ($\rho_X = \rho_Y = 1$) and only consistent with $\rho_X = 1$, $\rho_Y = 2.71$, agrees with our result. This value is also supported by the Stokes-Einstein model. The stickiness factor (S) calculated to be (0.0875) which is close to the slip limit (S = 0).

The anisotropic interaction parameter κ which is a measure of the anisotropy of intermolecular interactions, was found to be 0.15 for Cp_2VCl_2 in toluene. κ for VOAA in toluene is 0.53. The small κ value for Cp_2VCl_2 in toluene could be due to the absence of oxygen atom at the apex of a five coordination square pyramidal structure present in VOAA, resulting in a more slippery boundary condition. Therefore, it seems that κ value decreases with decreasing solute corrugation. So we expect that κ for VO[5-MeO-Sal SB](Phen) to be higher value.

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APPENDIX 1

```
FILE: DIF      OUTPUT   A1  KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS, DHAHRAN

C                                                                       DIF00010
C   THIS PROGRAM IS A SIMULATION FOR CACULATION OF THE TRANSLATION      DIF00020
C   DIFFUSION CONSTANTS THE EQUATIONS ARE TAKEN FROM THE FOLLOING       DIF00030
C   REFERENCE" JOURNAL OF MAGNETIC RESONANCE 22,289-293(1976)  "        DIF00040
C   BY THE TITEL " DIFFUSION COEFFICIENT OF PARAMAGNETIC SPECIES        DIF00050
C   IN SOLUTION " REPORTED BY " MYONG-KU AHN" .                         DIF00060
C   THE CAPILLARY DIFFUSION METHOD ARE USED AND MONITORING THE          DIF00070
C   INTENSITIES BY ESR MACHIN AS A FUNCTION OF TIME .                   DIF00080
C   NOTE :-                                                             DIF00090
C                                                                       DIF00100
C   1)THE INPUT ARE :(FRIEST READ STATMENT)                             DIF00110
C     READ THE NAME OF THE COMPUND                                      DIF00120
C   2)THE INPUT ARE :(SECOND READ STATMENT)                             DIF00130
C     SPIN=SPIN Q.# FOR THE ATOM IN THE SAMPLE                          DIF00140
C     IDAY=THE NUMBER OF PLOTS TAKEN                                    DIF00150
C     REFINT= TOTAL INTINESTY OF THE LINES IN THE REFERANCE SPECTRON    DIF00160
C     NFIT=THE WANTED FIT ORDER                                         DIF00170
C     LT= TOTAL LENGTH OF THE CAPILLARY                                 DIF00180
C     LS= LENGTH OF THE CAPILLARY IN THE CAVITY                         DIF00190
C    THE INPUT ARE :(THAERED READ STATMENT)                             DIF00200
C     EACH LINE FOR ONE SPECTRON DATA,THE ORDER OF INPUT DATA ARE       DIF00210
C     IRO=INTINSETY OF A REFRENCE LINE IN THE SPECTRON                  DIF00220
C     WLO=THE LINE WIEDTH OF THE REFRENCE LINE IN THE SPECTRON          DIF00230
C     T=TIME(SEC) OF THE PLOT TAKEN WITH RESPECT TO THE START OF EXP.   DIF00240
C     EI(K)=THE INTINSETY OF ALL LINES IN THE SPECTRON                  DIF00250
C                                                                       DIF00260
C   3) THE OUTPUT RESULTS ARE ON SEPARET TWO  FIELS                     DIF00270
C   4) THE PROGRAM FINED THE LEAST SQURE VALUE OF THE ALL PLOT AND      DIF00280
C     FROM WHICH IT CALCULATE THE EXP. VALUE OF THE                     DIF00290
C     DIFFUSION COEFFICIENT.                                            DIF00300
C   5) THE CALCULATED DIFFUSION COEFFICIENT VALUE CALCULATED BY CHANGINGDIF00310
C     THE R-VALUE ( R < 1 ) IN SUBROUTINE DIFSIN UNTIL YOU GET BEST FITDIF00320
C   6) ON PLOT DATA FILE THE PROGRAM GENARETE THE CAL. INTINESTY AND    DIF00330
C     THE TIME WHICH CAN BE USED AS DATA FOR PLOTING BY ICUSYS,THE      DIF00340
C     TIME IS SCALED BY DIVIDING IT BY 10E3 FOR PLOTING ONLY            DIF00350
C                                                                       DIF00360
C ----------------------------------------------------------------------DIF00370
C                                                                       DIF00380
C    WRITEN BY --------->        HASAN.B.BALIKHOYOR                     DIF00390
C                                                                       DIF00400
C ----------------------------------------------------------------------DIF00410
C                                                                       DIF00420
      DOUBLE PRECISION T,ISUM,X,Y,TM,SMDIF,MINSQR,VAR,STNDEV,           DIF00430
     1 ISM,DIF,YCAL,BB,R                                                DIF00440
      CHARACTER NAME*30                                                 DIF00450
      REAL LT,LS,IRO,IO                                                 DIF00460
      DIMENSION X(100),Y(100),EI(100),W(100),AVGW(100,20),BB(20),       DIF00470
     2 DIFSQR(100)                                                      DIF00480
      PI=3.1415926                                                      DIF00490
      ACCUR=0.00001                                                     DIF00500
      SCAL=100000                                                       DIF00510
C ---- FIRST READ-------------------------------------------------------DIF00520
      READ(5,16) NAME                                                   DIF00530
   16 FORMAT(A30)                                                       DIF00540
C ---- SECOND READ------------------------------------------------------DIF00550
      READ(5,*) SPIN,IDAY,REFINT,NFIT,LT,LS                             DIF00560
      R=LS/LT                                                           DIF00570
      NP=IDAY                                                           DIF00580
      M=(2*SPIN)+1                                                      DIF00590
      WRITE(6,3)                                                        DIF00600
    3 FORMAT('1')                                                       DIF00610
      WRITE(7,123)                                                      DIF00620
  123 FORMAT('1',' ', '401',' ','2')                                    DIF00630
      WRITE(7,321) IDAY                                                 DIF00640
  321 FORMAT(I4)                                                        DIF00650
      MM=1                                                              DIF00660
      DO 66 L=1,IDAY                                                    DIF00670
      Z=-SPIN                                                           DIF00680
      ISUM=0                                                            DIF00690
C------- - READ STATMENT THREE ---------------------------------------- DIF00700
      READ(5,*) IRO,WLO,T,(EI(K),K=1,M)                                 DIF00710
      IO=IRO/REFINT                                                     DIF00720
           DO 77 K=1,M                                                  DIF00730
              EI(K)=EI(K)/REFINT                                        DIF00740
              ISUM=ISUM+EI(K)                                           DIF00750
```

```
 77         CONTINUE                                                      DIF00760
               IF(ISUM.GT.1) GO TO 108                                    DIF00770
               JJ=88                                                      DIF00780
            DO 118 N=1,M                                                  DIF00790
               W(N)=WLO*((10/EI(N))**.5)                                  DIF00800
               AVGW((JJ),N)=W(N)                                          DIF00810
 118       CONTINUE                                                      DIF00820
      IF(ISUM.GT.1) GO TO 106                                            DIF00830
      PP=JJ+1                                                            DIF00840
 108  CONTINUE                                                           DIF00850
      X(L)=T                                                             DIF00860
      Y(L)=ISUM                                                          DIF00870
       IPL=L-1                                                           DIF00880
       TSCAL=T/SCAL                                                      DIF00890
      WRITE(7,100) TSCAL,ISUM                                            DIF00900
 100   FORMAT(2(4X,F16.5))                                               DIF00910
  66   CONTINUE                                                          DIF00920
       M=-SPIN                                                           DIF00930
      WRITE(6,15) NAME                                                   DIF00940
  15  FORMAT(/,'THE NAME OF THE SAMPLE IS ',A30)                         DIF00950
      WRITE(6,5) M                                                       DIF00960
   5  FORMAT(/,'THE NUMBER OF LINES = ',I4)                              DIF00970
       WRITE(6,102)                                                      DIF00980
 102   FORMAT(/,'        ','THE SPIN Q.#   ',' ',                        DIF00990
     1'THE AVERAGE LINE WIDTH ')                                        DIF01000
      WRITE(6,700)                                                       DIF01010
 700  FORMAT(' ')                                                        DIF01020
        DO 88 K=1,M                                                     DIF01030
           AVRGW=0                                                      DIF01040
              DO 99 N=1,JJ                                              DIF01050
                 AVRGW=AVRGW+AVGW(N,K)                                  DIF01060
  99          CONTINUE                                                  DIF01070
           AVRGW=AVRGW/JJ                                               DIF01080
           WRITE(6,92) M,AVRGW                                          DIF01090
  92       FORMAT(12X,F6.1,7X,F16.5)                                    DIF01100
           M=M+1                                                        DIF01110
  88    CONTINUE                                                        DIF01120
C                                                                       DIF01130
C  TO CAL. THE VAR = STN.DIV & LOWEST                                   DIF01140
C                                                                       DIF01150
      SMDIF=0                                                           DIF01160
C--------------CALLING SIMULATION TO FIND THE BEST FIT AND LEAST SQUARE DIF01170
C--------------VALUE                                                   DIF01180
      CALL SIM(NP,NFIT,X,Y,BB)                                          DIF01190
      WRITE(6,607)                                                      DIF01200
 607  FORMAT(//,'PL.#',4X,'TIME.SEC',7X,'EXP.INTI',7X                   DIF01210
     1 ,'CAL.INTI',7X,'SQUR.DIFF')                                      DIF01220
      WRITE(6,608)                                                      DIF01230
 608  FORMAT(' ')                                                       DIF01240
      DO 60 K=1,NP                                                      DIF01250
      ISM=0                                                             DIF01260
      DO 70 N=1,NFIT                                                    DIF01270
      YCAL=BB(N)*(X(K)**(N-1))                                          DIF01280
      ISM=ISM+YCAL                                                      DIF01290
 70   CONTINUE                                                          DIF01300
      DIF=(Y(K)-ISM)                                                    DIF01310
      DIFSQR(K)=(Y(K)-ISM)**2                                           DIF01320
      SMDIF=SMDIF+DIFSQR(K)                                             DIF01330
      WRITE(6,80) K,X(K),Y(K),ISM,DIFSQR(K)                             DIF01340
 80   FORMAT(I3,4D15.3)                                                 DIF01350
 60   CONTINUE                                                          DIF01360
      MINSQR=DIFSQR(1)                                                  DIF01370
      J=1                                                               DIF01380
      DO 111 I=2,NP                                                     DIF01390
           IF(DIFSQR(I).GT.MINSQR) GO TO 12                             DIF01400
           MINSQR=DIFSQR(I)                                             DIF01410
           J=I                                                          DIF01420
 12   CONTINUE                                                          DIF01430
111   CONTINUE                                                          DIF01440
      WRITE(6,81) J                                                     DIF01450
 81   FORMAT(//,'THE LEAST SQUARES FIT IS FOR THE PLT.#  =',I3)         DIF01460
      VAR=(SMDIF/(M-1))                                                 DIF01470
      STNDEV=VAR**(0.5)                                                 DIF01480
      WRITE(6,90) VAR                                                   DIF01490
 90   FORMAT(/,'T H E   V A R I A N C E= ',D15.5)                       DIF01500
      WRITE(6,91) STNDEV                                                DIF01510
 91   FORMAT(/,'THE STANDARD DEVIATION = ',D15.5)                       DIF01520
      ISUM=Y(J)                                                         DIF01530
      T=X(J)                                                            DIF01540
```

```
C--------CALLING TRSDIFF TO CAL.THE EXP.DIFFUSION COEFF. ------          DIF01550
      CALL TRSDIFF (PI,T,LT,R,ACCUR,ISUM,SCAL,DIFF,RINT)                 DIF01560
      WRITE(6,23)                                                        DIF01570
   23 FORMAT(//,'          TIME . SEC    INTENSITY        R-VALUE        DIF01580
     1     DIFF.COEF    ')                                              DIF01590
      WRITE(6,24) T,ISUM,R,DIFF                                          DIF01600
   24 FORMAT(/,' EXP.VAL  :,E10.4,F13.6,D20.6,D18.6)                     DIF01610
C---------CALLING DIFSIM TO GENERATE THE CALCULATED INTINSETY AND TIME   DIF01620
      CALL DIFSIM(R,LT,PI,ACCUR,SCAL,DIFF,BB)                            DIF01630
      CALL TRSDIFF (PI,T,LT,R,ACCUR,ISUM,SCAL,DIFF,RINT)                 DIF01640
      WRITE(6,996) T,RINT,R,DIFF                                         DIF01650
  996 FORMAT(/,' CAL.VAL  ',E10.4,F13.6,D20.6,D18.6)                     DIF01660
      WRITE(6,2)                                                         DIF01670
    2 FORMAT('1')                                                        DIF01680
      STOP                                                               DIF01690
      END                                                                DIF01700
C ***************************************************************************DIF01710
      SUBROUTINE TRSDIFF (PI,T,LT,R,ACCUR,ISUM,SCAL,DIFF,RINT)           DIF01720
      DOUBLE PRECISION T,ISUM,R                                          DIF01730
      REAL LT                                                            DIF01740
      DIFF=0.0                                                           DIF01750
      K=100000000                                                        DIF01760
            A=8/(PI*PI*R)                                                DIF01770
            DO 11 I=1,K                                                  DIF01780
              N=0                                                        DIF01790
              SUM=                                                       DIF01800
                 DO 22 J=1,100                                           DIF01810
                    EEE=(((((2*N)+1)**2)*(PI**2)*DIFF*T)/(R*(LT**2)))    DIF01820
                    B=((EXP(-EEE))/(((2*N)+1)**2))                       DIF01830
                    IF (B.LE.ACCUR) GO TO 33                             DIF01840
                    FFF=(((2*N)+1)*PI*R)/2                               DIF01850
                    C=SIN(FFF)                                           DIF01860
                    D=((-1)**N)*B*C                                      DIF01870
                    SUM=SUM+D                                            DIF01880
                    N=N+1                                                DIF01890
   22            CONTINUE                                                DIF01900
   33          CONTINUE                                                  DIF01910
               RINT=A*SUM                                                DIF01920
               IF (RINT.LE.ISUM) GO TO 44                                DIF01930
               DIFF=DIFF+0.1E-9                                          DIF01940
   11        CONTINUE                                                    DIF01950
   44        CONTINUE                                                    DIF01960
      RETURN                                                             DIF01970
      END                                                                DIF01980
C                                                                        DIF01990
C ***************************************************************************DIF02000
C                                                                        DIF02010
      SUBROUTINE DIFSIM(R,LT,PI,ACCUR,SCAL,DIFF,BB)                      DIF02020
      DOUBLE PRECISION BB,R                                              DIF02030
      DIMENSION BB(20)                                                   DIF02040
      REAL LT                                                            DIF02050
C     WRITE(6,613)                                                       DIF02060
C 613 FORMAT(//,'THIS IS SIMULATION DATA  TIME(E+5)  VS INTENSITIES ')    DIF02070
      WRITE(6,999)                                                       DIF02080
  999 FORMAT(' ')                                                        DIF02090
      WRITE(7,300)                                                       DIF02100
  300 FORMAT(' ','401')                                                  DIF02110
C                                                                        DIF02120
C CHANGE R-VALUE TO GET BEST FIT                                         DIF02130
C                                                                        DIF02140
      R=0.5700+00                                                        DIF02150
C                                                                        DIF02160
C                                                                        DIF02170
      T=0                                                                DIF02180
      A=8/(PI*PI*R)                                                      DIF02190
       DO 11 I=1,401                                                     DIF02200
         N=0                                                             DIF02210
         SUM=0                                                           DIF02220
              DO 22 J=1,50                                               DIF02230
                 EEE=(((((2*N)+1)**2)*(PI**2)*DIFF*T)/(R*(LT**2)))       DIF02240
                 B=((EXP(-EEE))/(((2*N)+1)**2))                          DIF02250
                 IF (B.LE.ACCUR) GO TO 33                                DIF02260
                 FFF=(((2*N)+1)*PI*R)/2                                  DIF02270
                   C=SIN(FFF)                                            DIF02280
                   D=((-1)**N)*B*C                                       DIF02290
                 SUM=SUM+D                                               DIF02300
                   N=N+1                                                 DIF02310
   22         CONTINUE                                                   DIF02320
   33    CONTINUE                                                        DIF02330
         RINT=A*SUM                                                      DIF02340
         TSCAL=T/SCAL                                                    DIF02350
```

```
          WRITE(7,100) TSCAL,RINT                                          DIF02360
  100     FORMAT(2(8X,F16.5))                                              DIF02370
C         WRITE(6,101) TSCAL,RINT                                          DIF02380
C 101     FORMAT(2(8X,F16.5))                                              DIF02390
            T=T+(0.05*SCAL)                                                DIF02400
   11   CONTINUE                                                          DIF02410
        RETURN                                                           DIF02420
        END                                                              DIF02430
C ***************************************************************************DIF02440
C                                                                        DIF02450
C       PROGRAM TO SOLVE SYSTEMS OF LINEARSIMUL-                         DIF02460
C       TANEOUS EQUATIONS USING IBM SUBROUTINE DGELS                     DIF02470
C                                                                        DIF02480
C       INPUT:  N  -  NUMBER OF DATA POINTS                              DIF02490
C               ND -  MAXIMUM DEGREE OF POLYNOMIAL                       DIF02500
C               (X(I),Y(I), I=1,N)  -  THE DATA POINTS                   DIF02510
C*************************************************************           DIF02520
C+++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++ DIF02530
      SUBROUTINE SIM(NP,NFIT,X,Y,BB)                                     DIF02540
      DOUBLE PRECISION X,Y,B,AUX,POL,A,BB                                DIF02550
      DIMENSION X(100),Y(100),B(20),A(210),AUX(20),BB(20)                DIF02560
      EXTERNAL POL                                                       DIF02570
      N=NP                                                               DIF02580
      ND=NFIT                                                            DIF02590
      M=2                                                                DIF02600
  150 M2=M-1                                                             DIF02610
      IF(M.NE.NFIT) GOTO 202                                             DIF02620
      WRITE(6,55) N,M2                                                   DIF02630
  202 CONTINUE                                                           DIF02640
      CALL FIT(M,N,X,Y,A,B,AUX,POL)                                      DIF02650
      IF(M.NE.NFIT) GOTO 203                                             DIF02660
      WRITE(6,33)                                                        DIF02670
  203 CONTINUE                                                           DIF02680
      DO 200 I=1,M                                                       DIF02690
      J=I-1                                                              DIF02700
      IF(M.NE.NFIT) GOTO 201                                             DIF02710
      BB(I)=B(I)                                                         DIF02720
  200 WRITE(6,44) J,B(I)                                                 DIF02730
  201 CONTINUE                                                           DIF02740
      M=M+1                                                              DIF02750
      IF(M.LE.(ND+1)) GO TO 150                                          DIF02760
   11 FORMAT(2I5)                                                        DIF02770
   15 FORMAT(/,' THE # OF DATA POINTS IS',I4,' AND THE MAXIMUM DEGREE OFDIF02780
     1 POLYNOMIAL FIT IS',I3,/)                                          DIF02790
   20 FORMAT('          I          X(I)          Y(I)',/)                DIF02800
   22 FORMAT(2D15.3)                                                     DIF02810
   23 FORMAT(I10,1PD15.3,1PD15.3)                                        DIF02820
   33 FORMAT(//,' THE COEFFICIENTS OF POLYNOMIAL ARE',/)                 DIF02830
   44 FORMAT(' ',8X,'A(',I1,')=',1PD11.3)                                DIF02840
   55 FORMAT(//,' THE # OF DATA POINTS IS',I3,4X,' THE DESIRED POLYNOMI DIF02850
     1AL FIT IS ',I2)                                                    DIF02860
      RETURN                                                             DIF02870
      END                                                                DIF02880
C                                                                        DIF02890
      SUBROUTINE FIT(M,N,X,Y,A,B,AUX,POL)                                DIF02900
      DOUBLE PRECISION X,Y,B,AUX,POL,A                                   DIF02910
      DIMENSION X(1),Y(1),A(1),B(1),AUX(1)                               DIF02920
      ITRAN(I,J)=(J*(J-1))/2+I                                           DIF02930
      DO 100 K=1,M                                                       DIF02940
      B(K)=0.DO                                                          DIF02950
      DO 100 I=1,N                                                       DIF02960
      B(K)=B(K)+Y(I)*POL(K,X(I))                                         DIF02970
  100 CONTINUE                                                           DIF02980
      DO 200 J=1,M                                                       DIF02990
      DO 200 K=J,M                                                       DIF03000
      A(ITRAN(J,K))=0.DO                                                 DIF03010
      DO 200 I=1,N                                                       DIF03020
      A(ITRAN(J,K))=A(ITRAN(J,K))+POL(K,X(I))*POL(J,X(I))                DIF03030
  200 CONTINUE                                                           DIF03040
      CALL DGELS(B,A,M,1,0.0001,IER,AUX)                                 DIF03050
      IF(M.NE.NFIT) GOTO 202                                             DIF03060
      WRITE(6,11) IER                                                    DIF03070
   11 FORMAT(/,' MESSAGE ERROR # FROM DGELS IS',I3,/)                    DIF03080
  202 CONTINUE                                                           DIF03090
      RETURN                                                             DIF03100
      END                                                                DIF03110
C                                                                        DIF03120
C                                                                        DIF03130
```

```
      FUNCTION POL(I,X)                                                 DIF03140
      DOUBLE PRECISION X,POL                                            DIF03150
      POL=X**(I-1)                                                      DIF03160
      RETURN                                                            DIF03170
      END                                                               DIF03180
C                                                                       DIF03190
C                                                                       DIF03200
C                                                                       DIF03210
C     ..................................................................DIF03220
C                                                                       DIF03230
C        SUBROUTINE DGELS                                               DIF03240
C                                                                       DIF03250
C        PURPOSE                                                        DIF03260
C           TO SOLVE A SYSTEM OF SIMULTANEOUS LINEAR EQUATIONS WITH     DIF03270
C           SYMMETRIC COEFFICIENT MATRIX UPPER TRIANGULAR PART OF WHICH DIF03280
C           IS ASSUMED TO BE STORED COLUMNWISE.                         DIF03290
C                                                                       DIF03300
C        USAGE                                                          DIF03310
C           CALL DGELS(R,A,M,N,EPS,IER,AUX)                             DIF03320
C                                                                       DIF03330
C        DESCRIPTION OF PARAMETERS                                      DIF03340
C           R      - DOUBLE PRECISION M BY N RIGHT HAND SIDE MATRIX     DIF03350
C                    (DESTROYED). ON RETURN R CONTAINS THE SOLUTION OF  DIF03360
C                    THE EQUATIONS.                                     DIF03370
C           A      - UPPER TRIANGULAR PART OF THE SYMMETRIC DOUBLE      DIF03380
C                    PRECISION M BY M COEFFICIENT MATRIX.  (DESTROYED)  DIF03390
C           M      - THE NUMBER OF EQUATIONS IN THE SYSTEM.             DIF03400
C           N      - THE NUMBER OF RIGHT HAND SIDE VECTORS.             DIF03410
C           EPS    - SINGLE PRECISION INPUT CONSTANT WHICH IS USED AS   DIF03420
C                    RELATIVE TOLERANCE FOR TEST ON LOSS OF             DIF03430
C                    SIGNIFICANCE.                                      DIF03440
C           IER    - RESULTING ERROR PARAMETER CODED AS FOLLOWS         DIF03450
C                    IER=0  - NO ERROR,                                 DIF03460
C                    IER=-1 - NO RESULT BECAUSE OF M LESS THAN 1 OR     DIF03470
C                             PIVOT ELEMENT AT ANY ELIMINATION STEP     DIF03480
C                             EQUAL TO 0,                               DIF03490
C                    IER=K  - WARNING DUE TO POSSIBLE LOSS OF SIGNIFI-  DIF03500
C                             CANCE INDICATED AT ELIMINATION STEP K+1,  DIF03510
C                             WHERE PIVOT ELEMENT WAS LESS THAN OR      DIF03520
C                             EQUAL TO THE INTERNAL TOLERANCE EPS TIMES DIF03530
C                             ABSOLUTELY GREATEST MAIN DIAGONAL         DIF03540
C                             ELEMENT OF MATRIX A.                      DIF03550
C           AUX    - DOUBLE PRECISION AUXILIARY STORAGE ARRAY           DIF03560
C                    WITH DIMENSION M-1.                                DIF03570
C                                                                       DIF03580
C        REMARKS                                                        DIF03590
C           UPPER TRIANGULAR PART OF MATRIX A IS ASSUMED TO BE STORED   DIF03600
C           COLUMNWISE IN M*(M+1)/2 SUCCESSIVE STORAGE LOCATIONS, RIGHT DIF03610
C           HAND SIDE MATRIX R COLUMNWISE IN M*N SUCCESSIVE STORAGE     DIF03620
C           LOCATIONS. ON RETURN SOLUTION MATRIX R IS STORED COLUMNWISE  DIF03630
C           TOO.                                                        DIF03640
C           THE PROCEDURE GIVES RESULTS IF THE NUMBER OF EQUATIONS M IS DIF03650
C           GREATER THAN 0 AND PIVOT ELEMENTS AT ALL ELIMINATION STEPS  DIF03660
C           ARE DIFFERENT FROM 0. HOWEVER WARNING IER=K - IF GIVEN -    DIF03670
C           INDICATES POSSIBLE LOSS OF SIGNIFICANCE. IN CASE OF A WELL  DIF03680
C           SCALED MATRIX A AND APPROPRIATE TOLERANCE EPS, IER=K MAY BE DIF03690
C           INTERPRETED THAT MATRIX A HAS THE RANK K. NO WARNING IS     DIF03700
C           GIVEN IN CASE M=1.                                          DIF03710
C           ERROR PARAMETER IER=-1 DOES NOT NECESSARILY MEAN THAT       DIF03720
C           MATRIX A IS SINGULAR, AS ONLY MAIN DIAGONAL ELEMENTS        DIF03730
C           ARE USED AS PIVOT ELEMENTS. POSSIBLY SUBROUTINE DGELG (WHICHDIF03740
C           WORKS WITH TOTAL PIVOTING) WOULD BE ABLE TO FIND A SOLUTION.DIF03750
C                                                                       DIF03760
C        SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED                  DIF03770
C           NONE                                                        DIF03780
C                                                                       DIF03790
C        METHOD                                                         DIF03800
C           SOLUTION IS DONE BY MEANS OF GAUSS-ELIMINATION WITH         DIF03810
C           PIVOTING IN MAIN DIAGONAL, IN ORDER TO PRESERVE             DIF03820
C           SYMMETRY IN REMAINING COEFFICIENT MATRICES.                 DIF03830
C                                                                       DIF03840
C     ..................................................................DIF03850
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C                                                                       DIFD3860
      SUBROUTINE DGELS(R,A,M,N,EPS,IER,AUX)                             DIFD3870
C                                                                       DIFD3880
C                                                                       DIFD3890
      DIMENSION A(1),R(1),AUX(1)                                        DIFD3900
      DOUBLE PRECISION R,A,AUX,PIV,TB,TOL,PIVI                          DIFD3910
      DIMENSION A(M),R(M),AUX(M)                                        DIFD3920
C                                                                       DIFD3930
C     SEARCH FOR GREATEST MAIN DIAGONAL ELEMENT                         DIFD3940
    1 IER=0                                                             DIFD3950
      PIV=0.D0                                                          DIFD3960
      L=0                                                               DIFD3970
      DO 3 K=1,M                                                        DIFD3980
      L=L+K                                                             DIFD3990
      TB=DABS(A(L))                                                     DIFD4000
      IF(TB-PIV)3,3,2                                                   DIFD4010
    2 PIV=TB                                                            DIFD4020
      I=L                                                               DIFD4030
      J=K                                                               DIFD4040
    3 CONTINUE                                                          DIFD4050
      TOL=EPS*PIV                                                       DIFD4060
C     MAIN DIAGONAL ELEMENT A(I)=A(J,J) IS FIRST PIVOT ELEMENT.         DIFD4070
C     PIV CONTAINS THE ABSOLUTE VALUE OF A(I).                          DIFD4080
C                                                                       DIFD4090
C                                                                       DIFD4100
C     START ELIMINATION LOOP                                            DIFD4110
      LST=0                                                             DIFD4120
      MM=M*M                                                            DIFD4130
      LEND=M-1                                                          DIFD4140
      DO 18 K=1,M                                                       DIFD4150
C                                                                       DIFD4160
C     TEST ON USEFULNESS OF SYMMETRIC ALGORITHM                         DIFD4170
      IF(PIV)20,20,4                                                    DIFD4180
    4 IF(IER)7,5,7                                                      DIFD4190
    5 IF(PIV-TOL)6,6,7                                                  DIFD4200
    6 IER=K-1                                                           DIFD4210
    7 LT=J-K                                                            DIFD4220
      LST=LST+K                                                         DIFD4230
C                                                                       DIFD4240
C     PIVOT ROW REDUCTION AND ROW INTERCHANGE IN RIGHT HAND SIDE R      DIFD4250
      PIVI=1.D0/A(I)                                                    DIFD4260
      DO 8 L=K,MM,M                                                     DIFD4270
      LL=L+LT                                                           DIFD4280
      TB=PIVI*R(LL)                                                     DIFD4290
      R(LL)=R(L)                                                        DIFD4300
    8 R(L)=TB                                                           DIFD4310
C                                                                       DIFD4320
C     IS ELIMINATION TERMINATED                                         DIFD4330
      IF(K-M)9,19,19                                                    DIFD4340
C                                                                       DIFD4350
C     ROW AND COLUMN INTERCHANGE AND PIVOT ROW REDUCTION IN MATRIX A.   DIFD4360
C     ELEMENTS OF PIVOT COLUMN ARE SAVED IN AUXILIARY VECTOR AUX.       DIFD4370
    9 LR=LST+(LT*(K+J-1))/2                                             DIFD4380
      LL=LR                                                             DIFD4390
      L=LST                                                             DIFD4400
      DO 18 II=K,LEND                                                   DIFD4410
      L=L+II                                                            DIFD4420
      LL=LL+1                                                           DIFD4430
      IF(L-LR)12,10,11                                                  DIFD4440
   10 A(LL)=A(LST)                                                      DIFD4450
      TB=A(L)                                                           DIFD4460
      GO TO 13                                                          DIFD4470
   11 LL=L+LT                                                           DIFD4480
   12 TB=A(LL)                                                          DIFD4490
      A(LL)=A(L)                                                        DIFD4500
   13 AUX(II)=TB                                                        DIFD4510
   18 A(L)=PIVI*TB                                                      DIFD4520
C                                                                       DIFD4530
C     SAVE COLUMN INTERCHANGE INFORMATION                               DIFD4540
      A(LST)=I*T                                                        DIFD4550
C                                                                       DIFD4560
```

```
C     ELEMENT REDUCTION AND SEARCH FOR NEXT PIVOT                    DIF04570
      PIV=0.D0                                                       DIF04580
      LLST=LST                                                       DIF04590
      LT=0                                                           DIF04600
      DO 18 II=K,LEND                                                DIF04610
      PIVI=-AUX(II)                                                  DIF04620
      LL=LLST                                                        DIF04630
      LT=LT+1                                                        DIF04640
      DO 15 LLD=II,LEND                                              DIF04650
      LL=LL+LLD                                                      DIF04660
      L=LL+LT                                                        DIF04670
   15 A(L)=A(L)+PIVI*A(LL)                                           DIF04680
      LLST=LLST+II                                                   DIF04690
      LR=LLST+LT                                                     DIF04700
      TB=DABS(A(LR))                                                 DIF04710
      IF(TB-PIV)17,17,16                                             DIF04720
   16 PIV=TB                                                         DIF04730
      I=LR                                                           DIF04740
      J=II+1                                                         DIF04750
   17 DO 18 LR=K,MM,M                                                DIF04760
      LL=LR+LT                                                       DIF04770
   18 R(LL)=R(LL)+PIVI*R(LR)                                         DIF04780
C     END OF ELIMINATION LOOP                                        DIF04790
C                                                                    DIF04800
C                                                                    DIF04810
C     BACK SUBSTITUTION AND BACK INTERCHANGE                         DIF04820
   19 IF(LEND)24,23,20                                               DIF04830
   20 II=M                                                           DIF04840
      DO 22 I=2,M                                                    DIF04850
      LST=LST-II                                                     DIF04860
      II=II-1                                                        DIF04870
      L=A(LST)+.500                                                  DIF04880
      DO 22 J=II,MM,M                                                DIF04890
      TB=R(J)                                                        DIF04900
      LL=J                                                           DIF04910
      K=LST                                                          DIF04920
      DO 21 LT=II,LEND                                               DIF04930
      LL=LL+1                                                        DIF04940
      K=K+LT                                                         DIF04950
   21 TB=TB-A(K)*R(LL)                                               DIF04960
      K=J+L                                                          DIF04970
      R(J)=R(K)                                                      DIF04980
   22 R(K)=TB                                                        DIF04990
   23 RETURN                                                         DIF05000
C                                                                    DIF05010
C                                                                    DIF05020
C     ERROR RETURN                                                   DIF05030
   24 IER=-1                                                         DIF05040
      RETURN                                                         DIF05050
      END                                                            DIF05060
```

CP2VCL2

3.5	57	11965	4	3.500		2.000				
1869	6.2622	240		1842	1756	1869	1816	1678	1427	1102	895
1775	6.2622	48000		1381	1671	1775	1774	1583	1406	1169	840
1765	6.2622	74400		1438	1666	1765	1752	1582	1346	1118	852
1805	6.2622	87600		1410	1684	1805	1716	1567	1363	1080	809
1693	6.6536	137700		1343	1642	1693	1660	1554	1253	1031	756
1666	6.6536	153300		1330	1614	1666	1676	1533	1272	1012	791
1648	6.2622	173100		1313	1586	1648	1597	1485	1282	1027	770
1616	5.8708	211500		1272	1508	1616	1620	1461	1157	976	726
1504	6.2622	240600		1242	1438	1504	1537	1345	1185	928	722
1528	5.8708	259200		1205	1477	1528	1546	1385	1161	935	723
1509	6.2622	297300		1168	1391	1509	1467	1363	1152	911	694
1442	6.2622	318300		1158	1381	1442	1489	1321	1117	868	700
1425	6.2622	345600		1134	1356	1425	1363	1221	1053	816	687
1386	6.2622	381300		1120	1352	1386	1394	1235	1026	839	651
1302	6.1057	409200		1070	1262	1302	1309	1194	1006	784	674
1313	5.9491	430500		1055	1237	1313	1311	1172	1003	781	595
1304	5.6360	468600		1011	1201	1304	1256	1181	936	772	577
1196	6.1057	498000		985	1160	1196	1195	1129	885	741	580
1196	5.9491	511800		988	1176	1196	1190	1092	917	691	555
1121	6.1057	555000		946	1128	1121	1178	1021	917	726	564
1104	5.7926	579000		883	1092	1104	1149	1057	837	695	558
1151	5.6360	604200		880	1044	1151	1073	1003	786	625	507
1090	6.1057	666900		796	979	1090	997	924	783	620	480
1002	5.4795	690000		824	934	1002	1061	885	751	605	443
1013	5.6360	726900		800	911	1013	964	862	724	569	415
933	6.2622	757500		803	912	933	927	819	752	525	446
918	5.4795	777600		758	875	918	931	820	688	586	383
863	5.9491	815100		721	813	863	908	796	665	512	375
877	5.0098	843000		684	837	877	849	798	662	527	392
839	6.1057	859800		651	767	839	840	790	643	505	370
847	5.9491	900600		628	765	847	776	780	628	466	377
726	5.7926	926700		615	799	726	757	692	558	472	369
754	5.6360	939600		597	777	754	719	689	565	445	331
706	6.2622	986900		619	725	706	700	673	539	445	320
720	5.6360	1011600		549	693	720	712	683	500	438	304
695	5.1663	1035000		555	675	695	672	651	470	412	310
690	5.7926	1072800		514	642	690	649	623	481	388	310
669	5.7926	1072800		480	627	669	620	542	446	387	269
700	5.9491	1116900		453	563	700	588	584	478	361	283
609	5.4795	1174500		407	615	609	580	539	432	284	275
568	5.7926	1194900		426	563	568	563	496	380	332	244
543	5.1663	1211400		443	555	543	581	503	436	345	278
506	5.0098	1246200		468	497	506	518	495	378	380	287
510	5.7926	1272600		421	508	510	516	499	411	316	219
521	5.1663	1295700		403	492	521	491	444	406	287	222
485	5.7926	1332300		367	470	485	528	429	379	324	202
498	5.6360	1362300		365	408	498	500	417	376	264	244
477	5.3229	1380900		368	457	477	458	363	320	262	220
444	5.4795	1419900		318	439	444	455	405	348	289	198
421	5.1663	1443900		358	410	421	418	328	328	222	177
383	5.1663	1468500		335	363	383	435	387	343	246	213
423	5.1663	1505100		359	388	423	407	365	335	230	200
416	5.4795	1547700		313	357	416	370	365	257	252	162
383	5.4795	1592100		306	356	383	337	308	244	227	180
286	5.6360	1693500		261	313	286	319	301	230	209	144
292	6.4188	1797360		234	286	292	229	210	194	190	174
235	5.6360	1878360		224	237	235	279	247	212	163	138

VO(5-MEO-SAL SB)(PHEN)
3.5 62 41684 5 3.500 2.000
7781 12.3940 480 3982 5965 7512 7781 6547 4781 3154 2002
7542 12.3940 36180 3841 5772 7288 7542 6381 4561 3069 1950
7428 12.3940 59580 3784 5637 7161 7428 6200 4466 3001 1892
7151 12.3940 87480 3647 5444 6874 7151 6010 4312 2881 1843
6854 12.3940 121980 3441 5191 6568 6854 5738 4104 2733 1733
6649 12.3940 147880 3345 5014 6376 6649 5600 3995 2648 1669
6410 12.3940 173580 3227 4872 6189 6410 5395 3859 2548 1604
6036 12.3940 208080 3051 4593 5799 6036 5091 3600 2409 1495
5914 12.3940 233880 2960 4511 5676 5914 4983 3552 2369 1505
5735 12.3940 259380 2871 4343 5515 5735 4793 3421 2279 1441
5423 12.3940 294780 2705 4098 5214 5423 4572 3254 2146 1343
5272 12.3940 321780 2632 4000 5087 5272 4423 3166 2084 1322
5078 12.3940 345780 2584 3896 4878 5078 4304 3052 2064 1248
4883 12.3940 379080 2435 3719 4710 4883 4095 2919 1938 1208
4719 12.3940 405780 2342 3569 4559 4719 3951 2810 1862 1159
4515 12.3940 432180 2269 3434 4355 4515 3771 2682 1812 1119
4339 12.3940 466680 2180 3265 4169 4339 3609 2584 1705 1071
4211 12.3940 487080 2101 3175 4032 4211 3531 2486 1659 1047
4034 12.3940 517980 2007 3066 3885 4034 3381 2406 1608 1018
3858 12.3940 562080 1879 2879 3678 3858 3227 2255 1516 915
3716 12.3940 577080 1843 2807 3578 3716 3100 2204 1472 919
3547 12.3940 604980 1767 2696 3434 3547 2976 2130 1436 877
3417 12.3940 640080 1673 2572 3283 3417 2869 2033 1318 841
3334 11.7817 665580 1604 2492 3169 3334 2800 1948 1267 817
3181 11.7817 692280 1528 2361 3020 3181 2629 1840 1221 773
2929 12.3940 751980 1422 2206 2831 2929 2468 1711 1154 701
2831 11.7817 777780 1373 2126 2733 2831 2377 1664 1110 689
2709 11.7817 813180 1332 2023 2618 2709 2270 1597 1050 630
2605 12.3940 841380 1270 1958 2518 2605 2194 1551 1015 595
2561 11.7817 864180 1259 1903 2413 2561 2104 1482 957 599
2324 11.7817 930480 1150 1743 2223 2324 1924 1388 878 543
2155 11.7817 985080 1076 1621 2067 2155 1778 1253 841 514
2103 11.7817 1007880 1019 1567 1991 2103 1786 1241 809 486
2032 11.7817 1036380 990 1517 1928 2032 1660 1154 779 513
1939 11.7817 1070580 922 1454 1863 1939 1622 1107 755 453
1828 11.7817 1115880 884 1355 1737 1828 1529 1095 695 425
1785 11.7817 1159380 844 1287 1662 1785 1404 979 697 438
1660 11.7817 1201980 807 1216 1562 1660 1366 968 636 380
1575 11.7817 1257780 756 1158 1486 1575 1279 868 614 347
1451 12.3940 1296780 695 1121 1398 1451 1226 847 582 356
1426 11.7817 1330380 690 1057 1341 1426 1177 822 564 338
1166 11.7817 1376280 630 1032 1262 1366 1119 761 500 331
1311 11.7817 1416780 608 961 1208 1313 1087 728 493 312
1266 11.7817 1454280 599 925 1132 1266 998 701 484 300
1231 11.7817 1503480 556 855 1136 1233 968 682 475 302
1180 11.7817 1541280 568 886 1092 1180 926 658 458 268
1122 11.7817 1589580 524 798 1053 1122 898 642 427 260
1087 11.7817 1611480 526 797 1044 1087 900 641 403 274
1075 12.3940 1635480 485 781 991 1075 896 637 422 260
987 11.7817 1676280 490 784 950 987 828 615 391 255
969 11.0898 1711980 466 786 932 969 804 582 377 229
999 12.3940 1720680 491 739 930 999 809 531 409 225
965 11.7817 1762380 448 717 907 965 769 589 359 219
917 11.7817 1794180 463 686 893 917 786 545 373 224
944 11.7817 1814280 449 697 883 944 768 541 375 230
921 11.7817 1849080 450 699 847 921 749 520 361 231
928 11.7817 1875480 456 681 885 928 780 513 356 225
845 11.0898 1938480 387 640 797 845 729 476 354 208
827 11.7817 1980780 423 638 804 827 721 482 337 205
870 11.7817 2021580 419 605 806 870 665 489 313 209
820 12.3940 2050080 386 623 788 820 692 498 310 224
813 11.7817 2140080 388 605 761 813 692 471 330 179

FILE: DIFFVCL OUTPUT A1 KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS, DHAHRAN

THE NAME OF THE SAMPLE IS CP2VCL2

THE NUMBER OF LINES = 8

THE SPIN Q.#	THE AVERAGE LINE WIDTH
-3.5	6.92724
-2.5	5.95245
-1.5	5.82001
-0.5	5.85751
0.5	6.14422
1.5	6.72765
2.5	7.52331
3.5	8.55231

THE # OF DATA POINTS IS 57 THE DESIRED POLYNOMI AL FIT IS 3

THE COEFFICIENTS OF POLYNOMIAL ARE

A(0)= 1.0170+00
A(1)= -7.852D-07
A(2)= 1.385D-13
A(3)= 1.827D-20

PL.#	TIME.SEC	EXP.INTI	CAL.INTI	SQUR.DIFF
1	0.240D+03	0.100D+01	0.102D+01	0.269D-03
2	0.480D+03	0.966D+00	0.979D+00	0.171D-03
3	0.744D+03	0.961D+00	0.959D+00	0.478D-05
4	0.876D+03	0.951D+00	0.949D+00	0.332D-05
5	0.138D+04	0.912D+00	0.911D+00	0.102D-05
6	0.153D+04	0.909D+00	0.900D+00	0.892D-04
7	0.173D+04	0.893D+00	0.885D+00	0.731D-04
8	0.212D+04	0.862D+00	0.857D+00	0.307D-04
9	0.241D+04	0.826D+00	0.836D+00	0.963D-04
10	0.259D+04	0.831D+00	0.823D+00	0.699D-04
11	0.297D+04	0.806D+00	0.796D+00	0.947D-04
12	0.318D+04	0.791D+00	0.781D+00	0.881D-04
13	0.346D+04	0.756D+00	0.763D+00	0.487D-04
14	0.181D+04	0.751D+00	0.736D+00	0.165D-03
15	0.409D+04	0.718D+00	0.720D+00	0.428D-05
16	0.431D+04	0.706D+00	0.706D+00	0.629D-06
17	0.469D+04	0.687D+00	0.681D+00	0.414D-04
18	0.498D+04	0.657D+00	0.662D+00	0.293D-04
19	0.512D+04	0.651D+00	0.653D+00	0.487D-05
20	0.555D+04	0.634D+00	0.627D+00	0.583D-04
21	0.579D+04	0.615D+00	0.612D+00	0.118D-04
22	0.604D+04	0.590D+00	0.597D+00	0.480D-04
23	0.667D+04	0.556D+00	0.560D+00	0.122D-04
24	0.690D+04	0.543D+00	0.547D+00	0.157D-04

25	0.727D+04	0.522D+00	0.526D+00	0.149D-04
26	0.758D+04	0.510D+00	0.509D+00	0.142D-05
27	0.776D+04	0.497D+00	0.498D+00	0.128D-05
28	0.815D+04	0.472D+00	0.478D+00	0.461D-04
29	0.843D+04	0.466D+00	0.464D+00	0.427D-05
30	0.860D+04	0.451D+00	0.455D+00	0.200D-04
31	0.901D+04	0.439D+00	0.435D+00	0.191D-04
32	0.927D+04	0.416D+00	0.422D+00	0.386D-04
33	0.940D+04	0.407D+00	0.416D+00	0.864D-04
34	0.986D+04	0.394D+00	0.394D+00	0.522D-08
35	0.101D+07	0.384D+00	0.383D+00	0.686D-06
36	0.104D+07	0.370D+00	0.373D+00	0.416D-05
37	0.107D+07	0.359D+00	0.356D+00	0.564D-05
38	0.107D+07	0.337D+00	0.356D+00	0.364D-03
39	0.112D+07	0.335D+00	0.338D+00	0.103D-04
40	0.117D+07	0.312D+00	0.315D+00	0.816D-05
41	0.119D+07	0.298D+00	0.307D+00	0.847D-04
42	0.121D+07	0.307D+00	0.301D+00	0.396D-04
43	0.125D+07	0.291D+00	0.288D+00	0.687D-05
44	0.127D+07	0.284D+00	0.279D+00	0.195D-04
45	0.130D+07	0.273D+00	0.271D+00	0.116D-05
46	0.133D+07	0.266D+00	0.259D+00	0.383D-04
47	0.136D+07	0.256D+00	0.250D+00	0.387D-04
48	0.138D+07	0.244D+00	0.244D+00	0.181D-06
49	0.142D+07	0.238D+00	0.233D+00	0.262D-04
50	0.144D+07	0.222D+00	0.227D+00	0.228D-04
51	0.147D+07	0.226D+00	0.220D+00	0.323D-04
52	0.151D+07	0.226D+00	0.211D+00	0.228D-03
53	0.155D+07	0.208D+00	0.201D+00	0.911D-04
54	0.159D+07	0.192D+00	0.191D+00	0.991D-06
55	0.169D+07	0.172D+00	0.173D+00	0.374D-06
56	0.180D+07	0.151D+00	0.159D+00	0.610D-04
57	0.188D+07	0.145D+00	0.151D+00	0.437D-04

THE LEAST SQUARES FIT IS FOR THE PLT.# = 34

THE VARIANCE= 0.687690D-03

THE STANDARD DEVIATION = 0.262240D-01

	TIME , SEC	INTENSITY	R-VALUE	DIFF.COEF
EXP.VAL	0.986HE+06	0.394410	0.5714290+00	0.5203500-05
CAL.VAL	0.986HE+06	0.394407	0.5700000+00	0.5207070-05

1

THE NAME OF THE SAMPLE IS VO(5-NEO-SAL SB)(PHEN)

THE NUMBER OF LINES = 8

THE SPIN Q.#	THE AVERAGE LINE WIDTH
-3.5	17.19795
-2.5	13.69622
-1.5	12.32136
-0.5	12.02574
0.5	13.19674
1.5	15.71477
2.5	19.20445
3.5	24.37782

THE # OF DATA POINTS IS 62 THE DESIRED POLYNOMI AL FIT IS 4

THE COEFFICIENTS OF POLYNOMIAL ARE

A(0)= 1.0150+00
A(1)= -1.2700-06
A(2)= 6.5180-13
A(3)= -1.4120-19
A(4)= 9.6000-27

PL.#	TIME.SEC	EXP.INTI	CAL.INTI	SQUR.DIFF
1	0.4800+03	0.1000+01	0.1010+01	0.2100-03
2	0.3620+05	0.9690+00	0.9700+00	0.5010-06
3	0.5960+05	0.9480+00	0.9420+00	0.4340-04
4	0.8750+05	0.9160+00	0.9090+00	0.4390-04
5	0.1220+06	0.8720+00	0.8700+00	0.7360-05
6	0.1470+06	0.8470+00	0.8420+00	0.2750-04
7	0.1740+06	0.8170+00	0.8140+00	0.1340-04
8	0.2080+06	0.7690+00	0.7780+00	0.6910-04
9	0.2340+06	0.7550+00	0.7520+00	0.9360-05
10	0.2590+06	0.7290+00	0.7270+00	0.4750-05
11	0.2950+06	0.6900+00	0.6940+00	0.1550-04
12	0.3220+06	0.6710+00	0.6690+00	0.4500-05
13	0.3460+06	0.6500+00	0.6480+00	0.4430-05
14	0.3790+06	0.6220+00	0.6200+00	0.3050-05
15	0.4060+06	0.5990+00	0.5980+00	0.1510-05
16	0.4120+06	0.5750+00	0.5770+00	0.4360-05
17	0.4670+06	0.5500+00	0.5500+00	0.2300-06
18	0.4870+06	0.5340+00	0.5350+00	0.2830-05
19	0.5180+06	0.5140+00	0.5130+00	0.1620-06
20	0.5620+06	0.4850+00	0.4830+00	0.3300-05
21	0.5770+06	0.4710+00	0.4730+00	0.1760-05
22	0.6050+06	0.4530+00	0.4550+00	0.7310-05
23	0.6400+06	0.4320+00	0.4340+00	0.2980-05

FILE: DIFFV6N OUTPUT A1 KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS, DHAHRAN

24	0.6660+06	0.4180+00	0.4190+00	0.2480-06
25	0.6920+06	0.3960+00	0.4010+00	0.5390-04
26	0.7520+06	0.3700+00	0.3720+00	0.2420-05
27	0.7780+06	0.3580+00	0.3590+00	0.1020-05
28	0.8130+06	0.3410+00	0.3410+00	0.1350-07
29	0.8410+06	0.3290+00	0.3280+00	0.9460-07
30	0.8640+06	0.3190+00	0.3180+00	0.1820-07
31	0.9300+06	0.2920+00	0.2910+00	0.1240-05
32	0.9850+06	0.2710+00	0.2700+00	0.6460-06
33	0.1010+07	0.2630+00	0.2620+00	0.4120-06
34	0.1040+07	0.2540+00	0.2530+00	0.9610-06
35	0.1070+07	0.2430+00	0.2420+00	0.1020-05
36	0.1120+07	0.2290+00	0.2280+00	0.1100-05
37	0.1160+07	0.2170+00	0.2160+00	0.1900-05
38	0.1200+07	0.2060+00	0.2050+00	0.1760-05
39	0.1260+07	0.1940+00	0.1920+00	0.4960-05
40	0.1300+07	0.1840+00	0.1830+00	0.8000-06
41	0.1330+07	0.1760+00	0.1760+00	0.1990-05
42	0.1380+07	0.1660+00	0.1660+00	0.2740-06
43	0.1420+07	0.1610+00	0.1610+00	0.1230-10
44	0.1450+07	0.1530+00	0.1550+00	0.2580-05
45	0.1500+07	0.1490+00	0.1480+00	0.7670-06
46	0.1540+07	0.1430+00	0.1430+00	0.4430-08
47	0.1590+07	0.1370+00	0.1370+00	0.3030-07
48	0.1610+07	0.1360+00	0.1350+00	0.1860-05
49	0.1640+07	0.1330+00	0.1320+00	0.8250-06
50	0.1680+07	0.1260+00	0.1280+00	0.3810-05
51	0.1710+07	0.1220+00	0.1250+00	0.5920-05
52	0.1720+07	0.1230+00	0.1240+00	0.1020-05
53	0.1760+07	0.1190+00	0.1210+00	0.2070-05
54	0.1790+07	0.1170+00	0.1180+00	0.1210-05
55	0.1810+07	0.1170+00	0.1170+00	0.1130-06
56	0.1850+07	0.1150+00	0.1150+00	0.5090-08
57	0.1880+07	0.1150+00	0.1130+00	0.3220-05
58	0.1940+07	0.1060+00	0.1090+00	0.7750-05
59	0.1980+07	0.1060+00	0.1070+00	0.2590-06
60	0.2020+07	0.1050+00	0.1030+00	0.4380-08
61	0.2050+07	0.1040+00	0.1040+00	0.1970-06
62	0.2140+07	0.1020+00	0.9950-01	0.4870-05

THE LEAST SQUARES FIT IS FOR THE PLT.# = 43

THE VARIANCE= 0.118950-03

THE STANDARD DEVIATION = 0.109060-01

	TIME , SEC	INTENSITY	R-VALUE	DIFF.COEF
EXP.VAL	0.1417E+07	0.160973	0.5714290+00	0.6763190-05
CAL.VAL	0.1417E+07	0.160970	0.6800000+00	0.6551420-05

APPENDIX 2

FILE: CPZZA OUTPUT AT KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS, DHAHRAN.

THE CAL. B & C VALUES FOR Z'=X USING STEWART & PORTE MAG.PAR FOR
DIFF. VALUES OF N, THE FREQ.=9.511 GHZ

CORR.TIME	B	C	
6.RRXIDE-12	.1641	.050078	
8.RRXIDE-12	.2Q0497	.07632	
Q.RRXIDE-11	.49759	.27855	N = 1
4.RRXIDE-11	.76488	.48681	
6.RRXIDE-11	1.04135	.69365	
8.RRXIDE-11	1.323	.899902	
SAME ORDER OF	.16137	.04914	
CORR.TIME AS	.177554	.064362	
ABOVE	.43962	.2344	N = 2
	.6642	.41236	
	.8954	.58926	
	1.1319	.765434	
	.12485	.0438045	
	.15765	.056191	
	.3904	.20361	
	.594456	.360114	N = 3
	.79416	.5161	
	.99882	.67187	
	.1120	.03872	
	.14296	.050582	
	.3683	.181913	N = 4
	.5452	.32381	
	.7227	.4641	
	.904694	.604434	

FILE: CPZZA OUTPUT AT KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS, DHAHRAN

THE CAL. B & C VALUES FOR Z'=Z USING STEWART & PORTE MAG.PAR FOR
DIFF. VALUES OF N, THE FREQ.=9.511 GHZ

CORR.TIME	B	C	
6.RRXIDE-12	.1641	.05808	
8.RRXIDE-12	.2045	.07632	
Q.RRXIDE-11	.4976	.27855	N = 1
4.RRXIDE-11	.76488	.48681	
6.RRXIDE-11	1.04135	.69365	
8.RRXIDE-11	1.323	.8999	
SAME ORDER OF	.2033	.078033	
CORR.TIME AS	.24982	.10315	
ABOVE	.60865	.37301	N = 2
	.96145	.64567	
	1.32433	.91678	
	1.6921	1.18812	
	.22996	.094192	
	.28013	.12483	
	.69651	.465711	N = 3
	1.11695	.7677237	
	1.54647	1.08928	
	1.9603	1.41183	
	.25085	.108362	
	.304077	.14372	
	.77282	.507559	N = 4
	1.25132	.87198	
	1.737758	1.236612	
	2.2281	1.6037	

FILE: CPZYA OUTPUT AT KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS, DHAHRA

THE CAL. B & C VALUES FOR Z'=Y USING STEWART & PORTE MAG.PAR FOR
DIFF. VALUES OF N, THE FREQ.=9.511 GHZ

CORR.TIME	B	C	
6.RRXIDE-12	.19846	.0725212	
8.RRXIDE-12	.24416	.09571	
Q.RRXIDE-11	.59542	.346568	N = 2
4.RRXIDE-11	.91819	.600999	
6.RRXIDE-11	1.29076	.854265	
8.RRXIDE-11	1.64822	1.10769	
SAME ORDER OF	.22173	.084427	
CORR.TIME AS	.27054	.11173	
ABOVE	.67318	.39953	N = 3
	1.0761	.68997	
	1.4876	.979926	
	1.9015	1.27856	
	.24004	.0950756	
	.29147	.12594	
	.741164	.465449	N = 4
	1.1961	.767255	
	1.65832	1.0694	
	.26904	.11394	
	.3253	.15006	
	.85929	.524855	N = 6
	1.4035	.90134	
	1.95282	1.27991	
	.292532	.13054	
	.35403	.172595	N = 8
	.96185	.593685	
	1.58272	1.01796	
	.348101	.172026	
	.42443	.226375	N = 10
	1.2163	.76435	
	.363874	.183978	
	.4449	.241789	N = 16
	1.2896	.81351	
	.39295	.20596	
	.46293	.2701	N = 20
	1.425	.9041	
	.45612	.2531	
	.56410	.33063	N = 30
	1.7151	1.0995	

THE CAL. B & C VALUES FOR Z' = X USING BAKALIK & HAYES MAG.PAR FOR DIFF. VALUES OF N, THE FREQ.=9.511 GHZ

CORR.TIME	B	C	
6.88X10E-12	.142395	.069719	
8.88X10E-12	.17748	.091617	
2.88X10E-11	.431849	.33435	N = 1
4.88X10E-11	.66343	.58424	
6.88X10E-11	.903776	.832302	
8.88X10E-11	1.1488	1.0795	
SAME ORDER OF	.13581	.079248	
CORR.TIME AS	.16832	.104483	
ABOVE	.43078	.37152	N = 4
	.6671	.64568	
	.90598	.919643	
	1.14861	1.19354	
	.13576	.094162	
	.16755	.12409	
	.856016	.82868	N = 8
	.7201	.780543	
	.98047	1.05478	
	1.2426	1.37079	

THE CAL. B & C VALUES FOR Z'= Y USING BAKALIK & HAYES MAG.PAR FOR DIFF. VALUES OF N, THE FREQ.=9.511 GHZ

CORR.TIME	B	C	
6.88X10E-12	.140063	.0602662	
8.88X10E-12	.171578	.0796071	
2.88X10E-11	.4170408	.2880488	N = 2
4.88X10E-11	.6629788	.4991802	
6.88X10E-11	.9159118	.709363	
8.88X10E-11	1.171911	.9197118	
SAME ORDER OF	.181371	.0808904	
CORR.TIME AS	.2189958	.1072044	
ABOVE	.5558927	.3789803	N = 4
	.9071857	.6522152	
	1.264618	.925948	
	1.624466	1.201343	
	.2507477	.1261718	
	.3030084	.1665878	N = 10
	.8418513	.5683533	
	1.402059	.9735658	
	.3792556	.221547	
	.470338	.289466	N = 30
	1.425019	.9633199	
	.6403737	.4096137	
	.8137168	.5314638	N = 100
	2.579395	1.770348	

THE CAL. B & C VALUES FOR Z'= Z USING BAKALIK & HAYES MAG. PAR FOR DIFF. VALUES OF N, THE FREQ.=9.511 GHZ

CORR.TIME	B	C	
6.88X10E-12	.14239	.069719	
8.88X10E-12	.17748	.091617	
2.88X10E-11	.43185	.33435	N = 1
4.88X10E-11	.66383	.58424	
6.88X10E-11	.903776	.832302	
8.88X10E-11	1.1488	1.07947	
SAME ORDER OF	.13586	.064047	
CORR.TIME AS	.168377	.08414	
ABOVE	.43088	.30049	N = 4
	.66732	.52604	
	.906382	.75188	
	1.14908	.976399	
	.13584	.066919	
	.16765	.087896	
	.45627	.30514	N = 8
	.72055	.53168	
	.98111	.76034	
	1.2434	.98986	

FILE: CP2XC OUTPUT A1 KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS, DHAHRAN

THE CAL. B & C VALUES FOR Z'=X USING CASEY & RAYNOR MAG.PAR. FOR
DIFF. VALUES OF N, THE FREQ.=9.511 GHZ

CORR.TIME	B	C	
6.88X10E-12	.20938	.051186	
8.88X10E-12	.260968	.067211	
2.88X10E-11	.63499	.28529	N = 1
4.88X10E-11	.97608	.42869	
6.88X10E-11	1.3289	.61084	
8.88X10E-11	1.6886	.7925	
SAME ORDER OF	.1857807	.03365571	
CORR.TIME AS	.1845777	.04388695	
ABOVE	.4753854	.1581491	N = 4
	.705093	.280999	
	.9357591	.4038153	
	1.172129	.5260099	
	.1118138	.02519779	
	.1425162	.03273453	
	.3889812	.1155009	N = 8
	.5730618	.2068584	
	.7467171	.2996178	
	.9226121	.3921521	

FILE: CP2ZC OUTPUT A1 KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS, DHAHRAN

THE CAL. B & C VALUES AT Z'= Z USING CASEY & RAYNOR MAG.PAR. FOR
DIFF. VALUES OF N, THE FREQ.=9.511 GHZ

CORR.TIME	B	C	
6.88X10E-12	.20938	.051186	
8.88X10E-12	.260968	.067211	
2.88X10E-11	.63499	.285297	N = 1
4.88X10E-11	.9761	.428694	
6.88X10E-11	1.3289	.61084	
8.88X10E-11	1.68859	.7924662	
SAME ORDER OF	.3298447	.09292165	
CORR.TIME AS	.3994029	.1232105	N = 4
ABOVE	1.014781	.4352556	
	1.64668	.748131	
	.8116183	.1318804	
	.8971032	.1738935	N = 8
	1.350281	.5976089	

FILE: CP2YC OUTPUT A1 KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS, DHAHRAN

THE CAL. B & C VALUES FOR Z'=Y USING CASEY & RAYNOR MAG.PAR FOR
DIFF. VALUES OF N, THE FREQ.=9.511 GHZ

CORR.TIME	B	C	
6.88X10E-12	.20938	.051186	
8.88X10E-12	.260968	.067211	
2.88X10E-11	.63499	.2853	N = 1
4.88X10E-11	.9761	.4287	
6.88X10E-11	1.3289	.61088	
SAME ORDER OF	.2947512	.0866697	
CORR.TIME AS	.358885	.1188427	N = 4
ABOVE	.911908	.4060238	
	1.467125	.698853	
	.3544578	.1202329	
	.4294979	.1590027	N = 8
	1.1670	.5467515	
	1.915462	.9369394	

FILE: CP2XD OUTPUT AT KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS, DHAHRAN

THE CAL. B & C VALUES FOR Z'=X USING PETERSEN & DAHL MAG.PAR AT
DIFF. VALUES OF N THE FREQ.=9.511 GHZ

CORR.TIME	B	C	
6.88X10E-12	.17839	.052638	
8.88X10E-12	.21736	.069172	
2.88X10E-11	.52889	.252457	N = 1.0
4.88X10E-11	.81300	.441216	
6.88X10E-11	1.10687	.6287	
8.88X10E-11	1.4065	.81567	
SAME ORDER OF	.123128	.0349899	
CORR.TIME AS	.155723	.0456389	
ABOVE	.4009#1	.168#11	N = 4.0
	.595986	.291979	
	.791918	.419518	
	.992593	.546438	
	.0959023	.026564#	
	.121981	.0345285	
	.332873	.121737	N = 8.0
	.492641	.217787	
	.6438828	.315219	
	.796998	.412501	

FILE: CP2YD OUTPUT AT KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS, DHAHRAN

THE CAL. B & C VALUES FOR Z'=Y USING PETERSEN & DAHL MAG.PAR AT
DIFF. VALUES OF N .THE FREQ.= 9.511 GHZ

CORR.TIME	B	C	
6.88X10E-12	.174392	.052638	
8.88X10E-12	.21736	.069172	N = 1
2.88X10E-11	.52889	.252457	
4.88X10E-11	.812997	.441216	
6.88X10E-11	1.10687	.5287	
8.88X10E-11	1.406#8	.81567	
SAME ORDER OF	.21706	.073773	
CORR.TIME AS	.26607	.097589	
ABOVE	.65864	.35019	N = 2.7
	1.04358	.605337	
	1.437498	.859878	
	.282285	.119276	
	.342421	.157710	N = 8
	.930494	.582482	
	1.52378	.930171	

FILE: CP2ZD OUTPUT AT KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS, DHAHRAN

THE CAL. B & C VALUES FOR Z'=Z USING PETERSEN & DAHL MAG.PAR FOR
DIFF. VALUES OF N , THE FREQ.=9.511 GHZ

CORR.TIME	B	C	
6.88X10E-12	17839	.052638	
8.88X10E-12	.21736	.0691718	
2.88X10E-11	.52889	.252457	N = 1
4.88X10E-11	.812997	.441216	
6.88X10E-11	1.10686	.6287	
8.88X10E-11	1.406455	.8156679	
SAME ORDER OF	.280983	.097772	
CORR.TIME AS	.3399639	.1296689	N = 4
ABOVE	.86351	.457974	
	1.403485	.78691	
	.353024	.139111	
	.4261	.18406	N = 8
	1.157812	.612495	
	1.91518	1.082584	

FILE: CP2Y27AL OUTPUT AT KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS, DHAHRAN

THE CAL B & C VALUES FOR Z'= Y AT N=2.7 USING DIFFERANTE MAG.PAR

CORR.TIME	B	C	
6.88X10E-12	.21542	.081018	
8.88X10E-12	.26338	.107161	
2.88X10E-11	.65111	.388558	STEWART & PORT
4.88X10E-11	1.03699	.6648	
6.88X10E-11	1.431913	.988381	
SAME ORDER	.15701	.068077	
CORR.TIME	.19095	.090098	
AS ABOVE	.470725	.323178	BAKALIK & HAYES
.	.75775	.558183	
.	1.05155	.792786	
8.88X10E-11	1.34814	1.02792	
	.267064	.073245	
	.32698	.09692	
	.80891	.34768	CASEY & RAYNOR
	1.28475	.60063	
	1.7717	.85295	
	.21706	.073773	
	.26607	.097589	
	.65864	.35019	PETERSEN & DAHL
	1.04358	.605337	
	1.437498	.859878	

FILE: CP2YDFRE OUTPUT AT KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS, DHAHRAN

THE CAL. B & C VALUES FOR Z'=Y AND N=2.7 AT DIFF.FREQ USING
MAG.PAR FOR PETERSEN & DAHL

CORR.TIME	B	C	
6.88X10E-12	.2131	.0736268	
8.88X10E-12	.261461	.097368	
2.88X10E-11	.64653	.34979	AT 9.3 GHZ
4.88X10E-11	1.0225	.60501	
6.88X10E-11	1.4072	.85962	
SAME ORDER	.21898	.073696	
OF CORR.TIME	.26365	.097473	
AS ABOVE FOR	.65227	.349982	AT 9.4 GHZ
ALL SETS	1.03247	.605168	
	1.4216	.85975	
	.21706	.073773	
	.26607	.097589	
	.65864	.35019	AT 9.511 GHZ
	1.04358	.605337	
	1.437498	.859878	
	.21872	.0738345	
	.268003	.097682	
	.663759	.350357	AT 9.6 GHZ
	1.05249	.605468	
	1.45028	.85998	
	.22058	.0739035	
	.270165	.0977856	
	.66951	.350538	AT 9.7 GHZ
	1.06251	.605612	
	1.4686	.860098	